Kinetic and mechanistic examinations of abiotic reductive transformation of halogenated methanes with bimetallic nano-scale particles

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**KINETIC AND MECHANISTIC EXAMINATIONS
OF ABIOTIC REDUCTIVE TRANSFORMATION OF
HALOGENATED METHANES WITH BIMETALLIC
NANO-SCALE IRON PARTICLES**

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SCHOOL OF CIVIL & ENVIRONMENTAL ENGINEERING

2007

ABIOTIC REDUCTIVE TRANSFORMATION WITH
BIMETALLIC NANO-SCALE IRON PARTICLES

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2007

**Kinetic and Mechanistic Examinations of Abiotic
Reductive Transformation of Halogenated
Methanes with Bimetallic Nano-scale Iron Particles**

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School of Civil & Environmental Engineering

A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
Doctor of Philosophy

2007

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ABSTRACT

Halogenated organic compounds (HOCs) are widely detected contaminants in polluted surface water and groundwater. Zero-valent Fe (ZVI) technology is a promising treatment method to deal with the HOCs. Due to some drawbacks of the ZVI technology, nano-scale bimetallic particles system has been developed in recent years. Although many studies on reductive dehalogenation of HOCs have been conducted over the last two decades, the mechanism involved remains rather elusive.

The main objectives of this study are to examine the kinetics, pathways and mechanisms of reductive dehalogenation reactions of chlorinated and brominated methanes with the nano-scale bimetallic particles. Both kinetic and mechanistic examinations are considered in establishing the major and minor transformation pathways. Meanwhile, the influences of pH, surfactant, natural organic matter, and nitrate on the dehalogenation kinetics were also investigated because these factors have direct impact on practical application of ZVI technology in treating polluted groundwater and wastewater.

Nano-scale Fe, Ni/Fe and Pd/Fe particles were synthesized by the wet chemical reduction method with sodium borohydride as the reductant. The nano-scale Ni/Fe and Pd/Fe particles were synthesized through co-reduction and post-coating method, respectively. The theoretical ratio of Ni to Fe in the synthesized nano-scale Ni/Fe particles was 1:4, while the Pd contents in the palladized Fe were 0.2% and 1% (w/w). The particle sizes were smaller than 100 nm, as observed with transmission electron microscope (TEM). The BET surface areas of the nano-scale particles were over one order higher than that of the commercial micro-scale Fe particles.

Batch reduction experiments were conducted to investigate reductive dehalogenation of the halogenated methanes with the two different types of the nano-scale bimetallic particles as well as with the nano-scale Fe and the commercial micro-scale Fe. The reductions of the target compounds were confirmed to follow pseudo-first order kinetics. The specific reduction rate constant for the transformation of carbon tetrachloride (CTC) with the Ni/Fe particles was $9.22 \times 10^{-2} \text{ l h}^{-1} \text{ m}^{-2}$ which was 13.2 times higher than that with the commercial micro-scale

Fe particles. The specific reduction rate of CTC with the 0.2% Pd/Fe particles was $1.61 \times 10^{-1} \text{ l h}^{-1} \text{ m}^{-2}$, which was even higher than that with the Ni/Fe particles. As the Pd content increased from 0.2% to 1%, it could further accelerate the reduction rate of the halogenated methanes for up to five times of the rate with the 0.2% Pd/Fe. Sodium borohydride was used to regenerate the aged nano-scale particles. The reactivities of the regenerated particles could be partially recovered to their fresh state.

The reduction of the halogenated methanes to end products could follow both parallel and sequential pathways. The main non-halogenated end product was found to be methane. However, the amount of methane produced was related to the type of zero-valent metals used. Based on the simulated reductive dehalogenation kinetics, CTC was found to reduce mainly through the hydrogenolysis pathway to chloroform (CF) with the nano-scale Ni/Fe or 0.2% Pd/Fe particles. On the other hand, the prominent reduction pathway of CF with the nano-scale bimetallic particles was through elimination to methane and other hydrocarbons. Dichloromethane (DCM) was usually persistent in the presence of the nano-scale bimetallic particles. In general, brominated methanes were more readily reduced than their chlorinated counterparts. The reductions of carbon tetrabromide (CTB) and bromoform (BF) were both mainly through the hydrogenolysis pathway. However, complete debromination of dibromomethane (DBM) to methane was the more favorable pathway compared to hydrogenolysis.

Linear free energy relationships (LFERs) were also established for the dehalogenation reactions of halogenated methanes. Based on the single-parameter LFERs, it was proposed that the first electron transfer process was the rate limiting step for both hydrogenolysis and elimination processes in the dehalogenation of brominated methanes. Based on the statistic analysis, two-parameter regression relationships were also established for the kinetics prediction for the dehalogenation reactions with the nano-scale Fe or Pd/Fe particles.

The existence of phosphate base buffer solution has inhibition effect on the dechlorination reaction. The inhibition effect of three anthropogenic surfactants on the dechlorination reaction followed the order: dodecyl pyridinium chloride (DPC) (cationic) > sodium dodecyl sulphate (SDS) (anionic) > nonylphenol ethoxylate

(NPE) (nonionic). Therefore, NPE was the most suitable surfactant for in-situ groundwater remediation and ex-situ soil wash process, if the recovered water is to be treated with nano-scale Fe particles. The appearance of higher nitrite concentration ($> 2\text{mM}$) could passivate the Fe surface and stall the dechlorination reaction. The regeneration of the aged nano-scale particles with sodium borohydride could only partial recover their original reactivity.

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ABBREVIATIONS

ANOVA	analysis of variance
bcc	body-centered cubic
BDE	bond dissociation energy
BET	Brunauer-Emmet-Teller
BF	bromoform
BM	bromomethane/methyl bromide/monobromomethane
BOCs	brominated organic compounds
CF	chloroform
CMC	critical micelle concentration
COCs	chlorinated organic compounds
DCA	dichloroethane
cDCE	cis-1,2dichloroethylene
CTB	carbon tetrabromide
CTC	carbon tetrachloride
DBM	dibromomethane
DCM	dichloromethane
DPC	dodecyl pyridinium chloride
E_1	one-electron reduction potential
E_2	two-electron reduction potential
E_{LUMO}	lowest unoccupied molecular orbital energies
EDX	energy dispersive x-ray analysis
fcc	face-centered cubic
FIA/IC	flow injection analyzer with ion chromatograph
FID	flame ionization detector
GC	gas chromatograph
GC/MS	gas chromatograph with mass selective detector
$[\text{H}]_{(\text{aq})}$	aqueous-phase H_2 concentration
HCA	hexachloroethane

HOCs	halogenated organic compounds
LFERs	linear free energy relationships
LHHW	Langmuir-Hinshelwood-Hougen-Watson model
LUMO	lowest unoccupied molecular orbital
NOMs	natural organic matters
NPE	nonylphenol ethoxylate
PRESS	prediction error sum of square
PCA	pentachloroethane
PCE	perchloroethylene
PRBs	permeable reactive barriers
SDS	sodium dodecyl sulfate
SEM	scanning electron microscope
SET	single electron transfer
TCA	trichloroethane
TCE	trichloroethylene
tDCE	trans-dichloroethylene
TeCA	tetrachloroethane
TEM	transmission electron microscope
VAEs	vertical attachment energies
VC	vinyl chloride
XANES	x-ray absorption near edge spectroscopy
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction
ZVI	zero-valent Fe

CHAPTER 1.

Introduction

1.1 Sources of Halogenated Organic Compounds and their Adverse Effects

Halogenated organic compounds (HOCs), including halogenated aliphatic compounds and halogenated aromatics, are widely used as solvents in degreasing, cleaning and extracting or as synthetic intermediates for plastic, herbicide and fire retardant chemicals. Due to the intensive usage of HOCs and their recalcitrance in natural environment, they appear to be ubiquitous groundwater and surface water contaminants. They are known as toxins and potential carcinogens. There are evidences that exposure to chlorinated aliphatics causes liver cancer in human beings. Short- and long-term exposures also affect human brain and kidneys, and in some cases cause damage to the developing fetus (Taniguchi et al., 2004; Sekizawa and Tanabe, 2005). Meanwhile, emission of HOCs from various activities can also lead to depletion of ozone layer. Ozone layer depletion is believed to lead to increasing skin cancer, eye diseases, possible disruptions and disorders of the immune systems, damage to vegetation, crops and building materials.

1.2 Possible Treatment Alternatives

To date, the stability and chemical inertness of many HOCs is part of their appeal in many industrial processes. However, these characteristics also make them slow to degrade once they are released into the environment. Since there are no natural sources of HOCs, almost no natural organisms had evolved to transform HOCs. Usually, hydrolysis has nothing to do with the xenobiotic of HOCs. Biodegradation of HOCs through natural aerobic and anaerobic processes to the less toxic non-halogenated products is also unfavorable. The persistence of HOCs has spurred an intensive effort to find their efficient and cost effective treatment method.

Two groups of contaminated sites and water treatment methods have been developed to treat HOCs, namely mass transfer and destructive transformation methods. The mass transfer mechanism can remove the HOCs from aqueous phase to other phases, which will then need further treatment or disposal. Destructive transformation can transform the HOCs to biodegradable or environmental benign products. Thus, it appears to be a better solution to HOCs treatment, and attracts more research interests. Aerobic cometabolism is a promising approach to destroy the less chlorinated compounds when certain aerobic microbes are supplied with methanol, toluene, or phenol (Kao and Prosser, 1999). However, the half lives of the HOCs through cometabolism process are usually in the order of months. Therefore, abiotic transformation can be an appealing alternative to the biological treatment method. The abiotic transformations include oxidative transformation and reductive transformation. Ozone is the most widely used oxidant for the oxidation process (Hirvonen et al., 2000). The main limitation of the oxidation methods is the less selectivity of the reactive intermediate hydroxyl radical produced from the decay of ozone, which can also react with many inorganic species (Yan and Schwartz, 1999). Usually, ozone can also be combined with UV to achieve a better oxidation performance. The high energy consumption is another drawback for the ozonation method. Permanganate has been proposed as an appealing alternative oxidant. It can only oxidize the chlorinated compounds with unstaturated carbon-carbon bond (e.g. trichlorethylene).

Besides the oxidation methods, the abiotic reductive transformation methods can also degrade most of the halogenated organics (Gillham and O'Hannesin, 1994; Schüth and Reinhard, 1998). The possible reductants include a variety of species, such as zero-valent metals (high hydrogen over-potential metals), hydrogen gas, iron (II), borohydride, hydrazine, etc. (Matheson and Tratnyek, 1994; Scrivanti et al., 1998; Hwang and Batchelor, 2002; Nutt et al., 2005). These reductants are associated with two reductive transformation methods, i.e. direct reduction with zero-valent metals and catalytic dehalogenation with Pd or other high hydrogen over-potential metals (e.g. Ni, At, Ag, Au etc.). It is generally believed that the ease of reductive dehalogenations of HOCs follows the sequence: $I > Br > Cl > F$. Considering the structure of substrate, the cleavage of the halogen-carbon bond is generally favored according to the following order: aliphatic < aromatic < vinylic < allylic < benzylic (Alonso et al., 2002). Generally, mono halides are more easily transformed through S_N2 mechanism, compared to the secondary and tertiary halides. However, the trend is opposite if the reaction occurred through S_N1 mechanism or with free radicals as the intermediate.

Among the zero-valent metals, zero-valent Fe (ZVI) is the most intensively studied metal for direct dehalogenation reaction, and has been successfully employed in groundwater remediation in the form of permeable reactive barrier. To improve the performance of ZVI, in recent years, the bimetallic particle system has been developed. In this system, a catalyst is introduced to enhance dechlorination process through catalytic effect. The bimetallic particle system can also limit the accumulation of the halogenated intermediates, and maintain the fresh surface condition of the zero-valent metal and prevent its passivation. The high reactivities of bimetallic particles make them attractive reactive material for groundwater and wastewater treatment.

1.3 Objectives and Scope of Work

Although ZVI technology has been proven to be effective for the HOCs transformation, thorough investigations of the pathway, mechanisms and the

influences of the solution matrix on dehalogenation of halogenated aliphatics with the nano-scale particle systems are still limited. To gain further insight in to the dehalogenation reactions with nano-scale bimetallic particles, the primary objectives of this research include thorough examination of transformation pathways, kinetics and mechanisms of halogenated methanes with Ni/Fe and Pd/Fe particles. The secondary objective of this study is to investigate the influences of solution matrix on the dechlorination reactions with nano-scale particles.

The scopes of this study include:

- (i) synthesizing nano-scale Fe, Ni/Fe and Pd/Fe particles and using various surface analytical tools for characterizing these nano-scale particles.
- (ii) examining the reduction pathways and dechlorination kinetics of halogenated methanes with the nano-scale particles in the batch reduction systems, and comparing the results with the commercial Fe and Zn.
- (iii) developing linear free energy relationships (LFERs) for the reduction of halogenated methanes with the nano-scale particles.
- (iv) observing the effects of solution matrix (e.g. pH, surfactant, natural organic matters, and nitrate) on the dechlorination kinetics.

1.4 Organization of Thesis

This thesis consists of seven chapters. The outline of the thesis is as follows:

- (i) Chapter 1 gives a brief introduction of sources of HOCs, their health effects on human beings, and their possible treatment methods. The main objectives and scopes of the work are also listed.
- (ii) Chapter 2 includes a detailed literature review of the abiotic reductive transformation methods for halogenated organic compounds, including direct reduction method with high hydrogen over-potential metal and catalytic hydrodehalogenation method with hydrogen donor.
- (iii) Chapter 3 describes the synthesis method and characterization of the nano-scale Fe and Ni/Fe particles. Transmission electron microscope (TEM) images and X-ray diffraction (XRD) patterns of the nano-scale Fe and Ni/Fe

particles are also shown in this chapter. The reduction kinetics and transformation pathways of various chlorinated methanes with the nano-scale particles are also observed. Meanwhile, performances the nano-scale particles were also compared with those of the commercial Fe and Zn powder.

- (iv) Chapter 4 presents the reduction products, kinetics, and transformation pathways of brominated methanes with the nano-scale Fe and Ni/Fe, and comparison are made to those with the commercial Fe powder.
- (v) Chapter 5 illustrates the synthesis method and characterization for the Pd/Fe particles. Based on the reduction rate constants, one-parameter linear free energy relationships (LFERs) for mechanism analysis are developed. Two-parameter regressions are also performed to get a primary approach for dechlorination rate prediction.
- (vi) Chapter 6 shows influences of the solution matrix (including pH, surfactants, natural organic matters, nitrate, nitrite, sulfate, and sulfite) and surface characterization of the regeneration nano-scale particles on the reduction kinetics of carbon tetrachloride.
- (vii) Chapter 7 outlines the main conclusions of this project. Recommendations for the future work are also presented.

CHAPTER 2.

Literature Review

2.1 Properties of Halogenated Aliphatics

Halogenated aliphatics, including carbon tetrachloride (CTC) and chloroform (CF), belong to an important group of halogenated organic compounds (HOCs), and are widely used as solvents in degreasing, cleaning and extracting or as synthetic intermediates for plastic and herbicides. Basically, most of the halogenated aliphatics are of high density and low water solubility. Once these contaminants enter groundwater systems, they will form pools at the bottom of the aquifer and continuously give off low-concentration contaminated plume. The physical and chemical properties of some halogenated methanes are shown in Table 2.1. The water solubility of halogenated aliphatics increases with increasing degree of halogenation. While, higher halogenated aliphatics shows higher density. Meanwhile, density of brominated aliphatics is higher than their chlorinated counterparts.

2.2 Zero-valent Metal Technology

In zero-valent metal technology, some metals, such as Fe, Zn and Mg etc., could be used as the reductants in the treatment system (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Boronina and Klabunde, 1995; Arnold and Roberts, 1998; Wüst et al., 1999; Mu et al., 2004; Volpe et al., 2004; Liu et al., 2005). Zero-valent Fe (ZVI) is the most intensively studied one among all the metals, because it is non-toxic to natural environment. The pH-pE plot (Fig. 2.1) shows the possibility of reduction of halogenated methanes with ZVI. ZVI for environmental remediation is typically applied in the form of permeable reactive barriers (PRBs). A PRB, as an in-situ passive remediation system, is a porous wall of granular iron which is constructed across the flow path of contaminated groundwater plume. When the contaminated groundwater passes through the reactive barrier, contaminants can be eliminated by the barrier (Fig. 2.2). The advantages of PRBs are (EPA, 1997): (i) limited maintenance and energy input after installation; (ii) no required surface structures except the monitoring wells; (iii) no change in the groundwater flow pattern as much as pump-and-treat system; (iv) no generation of wastes that need to be disposal of; (v) no mixing of contaminated and uncontaminated waters.

Fig. 2.1. pH-pE plot of halogenated methanes in the Fe/water system under conditions: $[Cl^-]=10^{-4}$ M, $[Br^-]=10^{-4}$ M, and $[Fe^{2+}]=[Fe^{3+}]=10^{-6}$ M.

Fig. 2.2. Schematic illustration of permeable reactive barriers (PRBs).

Fig. 2.3. Two basic designs of PRBs: (a) continuous trench system; (b) funnel-and-gate system (EPA, 1997).

Currently, two basic designs have been used for full scale installations, including continuous trench system and funnel-and-gate system (Fig. 2.3). The continuous trench (Fig. 2.3a) is a trench that has been excavated and simultaneously backfilled with reactive Fe, allowing the water to pass through the barrier under its natural gradient. In the funnel-and-gate system (Fig. 2.3b), an impermeable funnel is emplaced to enclose and direct the flow of contaminated water to a gate or gates containing the permeable zone of reactive Fe metal. The design prevents the contaminant plume from flowing around the barrier. Due to directing large amounts of water through a much smaller cross-sectional area of the aquifer, groundwater velocities within the PRB of funnel-and-gate system will be higher than those resulting from the natural gradient.

2.2.1 Reduction mechanisms

Gillham and O'Hannesin (1994) concluded that reductive degradation of halogenated aliphatics ($C_xH_yX_z$) by zero-valent metal is abiotic, heterogeneous, electrochemical reaction in which Fe is oxidized and halogenated aliphatics are reduced. Therefore, anodic and cathodic reactions are involved. The anodic reaction is as follows:

Halogenated aliphatics in anaerobic aqueous solution undergo reductive dehalogenation. The cathodic reaction can be expressed as:

There still exist other electron acceptors in the water-Fe system:

Obviously, ZVI is one of the reductants (electron donors) in this system, while the other reductants, Fe^{2+} and H_2 , are produced from the corrosion of iron powder in water (Eqs. 2.1 and 2.3). The presence of these reductants suggests three possible mechanisms that are responsible for the reduction of halogenated aliphatics, as expressed by Fig. 2.4.

Fig. 2.4. Three main mechanisms of HOCs reduction by ZVI (Matheson and Tratnyek, 1994).

The other two reductive half reactions are expressed as follows:

2.2.2 Kinetics study

Since dehalogenation reaction occurring at the iron and water interface is a heterogeneous process, mass transfer as well as reaction process must be involved (Matheson and Tratnyek, 1994). A general model for heterogeneous reactions often includes five steps (Stone and Morgan, 1990; Stumm, 1992): (i) transfer of the contaminant from bulk solution to metal surface; (ii) adsorption of the contaminant to the metal surface; (iii) reaction at the surface; (iv) desorption of products; and (v) transfer of the products from the surface to the bulk solution. The slowest reaction step controls the overall reaction kinetics.

(a) Influence of mass transfer

Determination of the rate-limiting process is a very important step for the analysis of a heterogeneous reaction. Three criteria can be used to identify the reaction limiting process of the dehalogenation reaction, including (i) weak contribution of the mixing speed to the reduction rate constant for the batch reduction system, (ii) higher activation energies of reaction limiting process than that of the mass transfer limiting process ($> 15 \text{ kJ mol}^{-1}$), and (iii) lower reaction rate constant than the surface-area normalized mass transfer coefficient. (Matheson and Tratnyek, 1994; Arnold et al., 1999; Su and Puls, 1999; Loraine et al., 2002). Based on the first criterion, many researchers indicated that the reduction of halogenated aliphatic with ZVI was controlled by reaction limiting step (Matheson and Tratnyek, 1994; Su and Puls, 1999). However, Arnold et al. (1999) indicated that the reductions of polychlorinated ethanes with Zn were controlled by mass transfer process, even though the rate constants were unaffected by the mixing rate. Thus, the other two criteria can be applied to give a valid conclusion of the rate limiting step. The activation energies in the second criterion can be calculated from Arrhenius Equation, shown as follows:

$$\ln k_{SA} = \ln A - E_a/RT \quad (2.7)$$

where R is the molar gas constant ($0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (K), A is preexponential factor ($\text{l h}^{-1} \text{ m}^{-2}$), and k_{SA} is specific reaction rate constant ($\text{l h}^{-1} \text{ m}^{-2}$). As referred in the third criterion, the over-all reaction rate can be represented as:

$$\frac{1}{k_{\text{overall}}} = \frac{1}{\alpha} \left(\frac{1}{k_L} + \frac{1}{k_{SA-\text{geom}}} \right) \quad (2.8)$$

where k_L is the mass transfer coefficient (m s^{-1}), α is the ratio of metal surface area to the volume of solution (m^{-1}) and $k_{SA-\text{geom}}$ is a rate constant for the surface reaction

on the basis of the external surface area of the particles (Arnold et al., 1999). An empirical formula, based on the boundary layer theory, can be used to estimate the k_L for packed bed reaction system (Harriott, 1962; Arnold et al., 1999, Loraine et al., 2002):

$$\frac{k_L \cdot d_p}{D_{AB}} = 2 + 0.6 \text{Re}^{1/2} \text{Sc}^{1/3} \quad (2.9)$$

where d_p is the diameter of particle (m), and D_{AB} is the binary diffusion coefficient ($\text{m}^2 \text{s}^{-1}$). The Reynold number (Re) and Schmidt number (Sc) in this equation can be expressed as follows:

$$\text{Re} = \frac{d_p \cdot U}{\nu} \quad (2.10)$$

$$\text{Sc} = \frac{\nu}{D_{AB}} \quad (2.11)$$

where U is the terminal velocity (m s^{-1}), ν is kinematic viscosity of liquid ($\text{m}^2 \text{s}^{-1}$). Mass transfer rates will increase with the decrease of the diameter of reactant particle. Therefore, decreasing the particle size can eliminate the influence of mass transfer process (Arnold et al. 1999; Lien, 2000). Lien (2000) also confirmed this conclusion in the dehalogenation reactions with nano-scale particles, in which the surface reaction step was concluded as the rate limiting step for most of the halogenated aliphatics investigated.

In a well mixed system (over 50 rpm), mass transfer is rapid and its effect on reaction rate can be ignored. Usually the heterogeneous reaction can be simplified to involving three steps as represented by the following diagram (Fig. 2.5).

Fig. 2.5. Three-step surface reaction model.

(b) Kinetics for the reaction limiting process

Combined zero- and first-order model can be used for depicting the kinetics of halogenated organic compounds (HOCs) reduction with ZVI (Fredrichson and Gorby, 1996; Johnson et al., 1996; Wüst et al., 1999). The model is expressed as follows:

$$\frac{dC}{dt} = -\frac{V_m C}{K_{1/2} + C} \quad (2.12a)$$

where

$$V_m = \Gamma \cdot \rho_a \cdot k_r \quad (2.12b)$$

$$K_{1/2} = \frac{k_b + k_r}{k_f} \quad (2.12c)$$

C is the aqueous concentration of parent compound (mol l^{-1}), V_m is the maximum reaction rate ($\text{mol l}^{-1} \text{s}^{-1}$), $K_{1/2}$ is the concentration of half maximum reaction rate concentration (mol l^{-1}) of reactive sites, ρ_a is the surface area concentration of iron ($\text{m}^2 \text{l}^{-1}$), k_b is dissociation rate constant (h^{-1}), k_f is association rate constant ($\text{l mol}^{-1} \text{h}^{-1}$), and k_r is reduction rate constant (h^{-1}).

In this model, at low substrate concentration ($C \ll K_{1/2}$), the reaction kinetics model becomes first order.

$$\frac{dC}{dt} = -\frac{V_m}{K_{1/2}} C = -k_{1.\text{obs}} C = k_{SA} \rho_a C \quad (2.13)$$

where $k_{1,obs}$ is the observed first-order rate constant (h^{-1}), and k_{SA} is the specific reaction rate constant ($l\ h^{-1}\ m^{-2}$). Many researches have confirmed that degradation of HOCs follows pseudo-first-order with respect to the decay of parent compounds (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Wüst et al., 1999; Burrow et al., 2000).

While at high concentration ($C \gg K_{1/2}$), the reaction sites are saturated by the HOCs and thus the reaction kinetic model can be simplified to zero-order kinetic model:

$$\frac{dC}{dt} = -V_m = -k_{0,obs} \quad (2.14)$$

where $k_{0,obs}$ is zero-order rate constant ($mol\ h^{-1}\ l^{-1}$). The suitability of zero-order kinetic model has also been confirmed by Orth and Gillham (1996).

For the surface-reaction limited case, a hyperbolic relationship between the initial rate and initial concentration can be observed. The Langmuir-Hinshelwood-Hougen-Watson (LHHW) model can be expressed as follows (Arnold and Roberts, 2000):

$$\frac{dC_i}{dt} = -\frac{\sum_{j=1}^{N_j} (k_{ij}^S S_t) K_i C_i}{1 + \sum_{m=1}^{N_m} K_m C_m} = -k_{obs} C_i \quad (2.15)$$

where k_{ij}^S is kinetic constant for a given surface limited reaction (h^{-1}), S_t is the abundance of reactive site per liter solution (μM), K is the adsorption constant for Langmuir type adsorption (μM^{-1}). The subscript i represents the parent species and N_j is the total number of primary products produced directly from parent compound i . N_m is the total number of compounds which can inhibit the reaction of parent compound. Because the concentration of parent compound is included in the denominator, the first-order rate constant changes with the concentration of the

parent compound in addition to other intermediate species which also compete for reaction site.

(c) Kinetics of sorption and desorption limiting process

In a packed-bed reactor, assuming the desorption of the dechlorinated products from the metal surface is not the rate-limiting process, the observed rate constants of the aqueous solute will depend on the adsorption and desorption rate and the surface reaction rate of the solute, as illustrated by the following equation (Loraine et al., 2002):

$$k_{\text{obs}} = -k_{\text{mt}} a C_{\text{aq}} - k_1 a C_{\text{surf}} \quad (2.16)$$

where k_{mt} is the rate constant of sorption ($\text{m}^3 \text{m}^{-2} \text{s}$), k_1 is the rate constant of the surface reaction ($\text{m}^3 \text{m}^{-2} \text{s}$), a is the ratio of solid surface area to liquid volume ($\text{m}^2 \text{m}^{-3}$), and C_{surf} is the concentration of solute sorbed to the solid surface (mol m^{-2}). Once the rates of transfer to and from the sorption sites are equal, the system is in equilibrium and the overall adsorption and desorption is zero. Thus, the observed reduction rate constants are only related to the surface reaction rate.

Based on the simplified LHHW model, the adsorption-limited kinetic model can be expressed as following (Arnold and Roberts, 2000):

$$\frac{dC_i}{dt} = - \frac{\left(\sum_{j=1}^{N_j} k_{ij}^a S_t \right) C_i}{1 + \sum_{m=1}^{N_m} K_m C_m} = -k_{\text{obs}} C_i \quad (2.17)$$

where k_{ij}^a is rate constant for adsorption-limited reaction ($\mu\text{M}^{-1} \text{h}^{-1}$), S_t is the amount of reactive site per liter solution (μM), and K is the adsorption constant for Langmuir adsorption isotherm (μM^{-1}).

For the desorption-limited reaction, the rate can be expressed as follow (Arnold and Roberts, 2000):

$$\frac{dC_i}{dt} = - \left(\sum_{j=1}^{N_j} k_{ij}^d S_t \right) \quad (2.18)$$

The rate-controlling step can be identified by checking the relationship between the initial concentration and the initial rate constant (Arnold and Roberts, 2000). For adsorption-limited reaction, the initial rate has a linear relationship with the initial concentration. While for a desorption-limited reaction, the initial rate remained constant with the initial concentration. The better fit of this simplified LHHW model with experimental data indicted the existence for the intraspecies competition for reactive sites at the metal surface (Arnold and Roberts, 2000).

(d) Fe dissolution kinetics and pH influence on the kinetics

The kinetics of Fe dissolution has been reported as a zero-order reaction (Fredrichson and Gorby, 1996):

$$\frac{dC_{Fe^{2+}}}{dt} = k_{obs(Fe^{2+})} = k_{SA(Fe^{2+})} \rho_a \quad (2.19)$$

where $k_{obs(Fe^{2+})}$ is the observed zero-order rate constant ($M h^{-1}$), $k_{SA(Fe^{2+})}$ is specific reaction rate constant of iron ($M h^{-1} l m^{-2}$), and ρ_a is the surface area concentration of Fe in solution ($m^2 l^{-1}$). The zero-order kinetics illustrates that the rate of dissolution of Fe is limited by dissociation from the steady state reactive surface complex. Fredrichson and Gorby (1996) found that in the presence of CTC, the corrosion rate of Fe apparently increased. At low concentration of CTC, the Fe corrosion rate increased with the increase of the CTC concentration. At high CTC concentration (over 0.5 mM), the rate reached a constant with further increase of CTC concentration.

In the ZVI system, pH is an important parameter influencing the reduction rate of HOCs and dissolution rate of ZVI. Since the proton is involved in all of the three reductive transformation mechanisms illustrated in Fig. 2.4, the pH value should have some influence on the reduction kinetics of HOCs. Matheson and Tratnyek (1994) showed that the change of pH value in the aqueous solution of water/Fe system during the reduction of CTC was usually within 1 unit. The minor fluctuation of pH would not show much influence on the dehalogenation rate. Thus, many researchers observed the reduction kinetics of HOCs in the ZVI system without adding buffer solution (Matheson and Tratnyek, 1994; Dayan et al., 1999; Su and Puls, 1999; Alessi and Li, 2001; Elliott and Zhang, 2001; Wang and Farrell, 2003; Xu et al., 2005^{a, b}).

To determine the dehalogenation rate over a wide range of pH value, buffer solution can be used to stabilize the pH value (Matheson and Tratnyek, 1994; Weber, 1996; Arnold et al., 1999; Arnold and Roberts, 2000; Song and Carraway, 2005). Matheson and Tratnyek (1994) reported that observed reduction rate constants of CTC dechlorination decreased with the increased pH ($5.5 < \text{pH} < 10.0$) and the relationship between the observed reduction rate constants and pH was approximately linear. Chen et al. (2001) observed that the specific reduction rate constant of TCE at pH 1.7 was about one order higher than that at pH 3.8, and generally the reduction rate decreased linearly with the increase in pH value. Meanwhile, corrosion rate of Fe showed the same trend as TCE reduction rate. Thus, extremely low pH ($\text{pH} < 3.8$) is not beneficial to the longevity of Fe.

2.2.3 Linear free energy relationships

Reductive dehalogenation usually occurs via two pathways, including hydrogenolysis pathway (replacement of halogen by hydrogen) and reductive elimination (simultaneous removal of two halogens). Reductive elimination includes: α -elimination (removal of two halogens from the same carbon to form carbene intermediate) and β -elimination (removal of two halogens from vicinal

carbon resulting in the increase of bond order). All these pathways involve transfer of electrons from the electron donor to the halogenated compounds (electron acceptor).

Theoretically, reductive dehalogenation can proceed either via single electron transfer (SET) mechanism (which may occur via outer sphere or inner sphere reactions) or a concerted two-electron transfer mechanism (which must necessarily be inner sphere) (Eberson, 1987; Totten et al., 2001). In an outer sphere reaction, no bond is broken or formed. The out-sphere reaction requires only physical adsorption of substrate and less interaction energy ($< 4 \text{ kJ mol}^{-1}$). While, the inner sphere reactions involve bond breaking, molecular rearrangement, or chemisorption of substrate on metal surface. Eberson (1987) indicated that since the outer sphere reaction represents the energetically less favorable pathway for electron transfer, outer sphere SET reduction pathway is rare in organic chemistry. Reactions occurred via SET step will result in the formation of radicals, while reactions occurred via concerted two-electron transfer pathways will result in the formation of closed shell products (β -elimination) or carbene intermediates (α -elimination). The selectivity of these two reaction pathways can give much influence on the distribution of products.

Many researchers have pointed out that the reduction of halogenated aliphatic compounds reaction undergoes SET pathway as follows:

It is usually initiated by dissociative electron transfer for x in between 0 and 2 (Matheson and Tratnyek, 1994; Balko and Tratnyek, 1998; Totten et al., 2001; Bylaska et al., 2002).

Because the formation of radicals is an irreversible process, it is not a complete outer sphere mechanism (Totten et al., 2001). The second electron transfer process

following after the reaction in Eq. 2.20 will transform the radical to a neutral hydrogenolysis product:

Alternatively, the radical can undergo another dissociative electron transfer to form carbenes or double-bond closed shell molecule. Balko and Tratnyek (1998) indicated that the concerted two electron transfer process for reductive elimination is thermodynamically favored over the SET process.

Transition state theory indicates that the relationship between the reaction rate constant and the energy required to reach a postulated transition state is expressed as following equation (Liu et al., 2000):

$$k_{\text{SA}} = A e^{\left(-\frac{\Delta G^*}{RT} \right)} \quad (2.22)$$

where ΔG^* (J mol^{-1}) is the activation energy for the transition intermediate which represents the rate limiting step in the overall reduction pathway, and A is the reaction-dependent preexponential factor. Marcus theory associated the activation energy (ΔG^*) with the corrected standard free energy change for the reaction ($\Delta G^{0'}$) (kJ mol^{-1}) (Curtis, 1991; Totten, 1999) as follows:

$$\Delta G^* = \frac{\lambda}{4} \left(1 + \frac{\Delta G^{0'}}{\lambda} \right)^2 \quad (2.23)$$

where λ is the reorganization energy (kJ mol^{-1}). Thus, combining the Eqs. 2.22 and 2.23 and taking the logarithm on both sides, there will be a parabolic relationship between $\log k_{\text{SA}}$ and $\Delta G^{0'}$.

$$\log k_{\text{SA}} = \log A - \left(\frac{1}{RT} \right) \left(\frac{\lambda}{4} \right) \left(1 + \frac{\Delta G^{0'}}{\lambda} \right)^2 \quad (2.24)$$

Over a limited range of $\Delta G^{0'}$, the linear regression could be used to establish the approximate relationship between the $\log k_{\text{SA}}$ and $\Delta G^{0'}$ (Totten, 1999). However, the main assumption of Marcus theory is that the associated electron transfer processes are through outer sphere pathways. Since the formation of radical is an irreversible process, the out-sphere pathway is less possible for the reductive dehalogenation reaction (Curtis, 1991; Totten, 1999). Although the assumption of Marcus theory cannot be upheld, the linear relationship between $\log k_{\text{SA}}$ and $\Delta G^{0'}$ or one-electron reduction potentials (E_1) can still be approximately applied (Scherer et al., 1998; Totten, 1999; Liu et al., 2000). Besides E_1 , several other predictor parameters, such as two-electron reduction potentials (E_2), hemolytic bond dissociation energy (BDE) and the lowest unoccupied molecular orbital energy (LUMO) etc., can also be used as the descriptors. The thermodynamic parameters used in the references above cited are listed in Table 2.2. The values of these thermodynamic parameters are given in Table 2.3.

Table 2.2 Definition of thermodynamic parameters

Name	Abbr.	Definition
One- electron Reduction Potential ^{a b c d e}	E ₁	The potential of the rate limiting initial electron-transfer step
Two- electron Reduction Potential ^{a b c d e}	E ₂	Overall reduction potential of net two electron transfer
Lowest Unoccupied Molecular Orbital Energies ^{b c}	E _{LUMO}	Energy with which electron transfer takes place at frontier molecular orbital
Vertical Attachment Energies ^f	VAEs	Positive electron impact energy at which an electron can be added to a molecule
Bond Dissociation Energy ^{c d} (Bond Strength ^e)	BDE	Energy needed to break carbon halogen bond to form carbon centered radical and atomic halogen

Note: a. Roberts et al., 1996; b. Scherer et al., 1998; c. Totten, 1999; d. Liu et al., 2000 ; e. Lien, 2000 ; f. Burrow et al., 2000

Table 2.3 The kinetic rate constants and thermodynamic constants of halo-aliphatics

compounds	k_{SA}^a ($Lm^{-2}h^{-1}$)	bond		E_{LUMO}^c (eV)	E_1^d (V)	$E_2(V)^e$		VAE ^f (eV)
		strength ^b (kJ/mol)				E_{2h}^h	E_{2r}^h	
CT	$(1.2 \pm 1.5) \times 10^{-1}$	305.9	-3.054	0.13		0.67		-0.34
CF	$(9.2 \pm 7.3) \times 10^{-4}$	338.5	-2.277	-0.23		0.56		0.35
DCM		350.2				0.49		
PCE	$(2.1 \pm 2.7) \times 10^{-3}$	389.6	-1.689	-0.36		0.582	0.631	0.30
TCE	$(3.9 \pm 3.6) \times 10^{-4}$	388.5	-1.435	-0.58 ^g		0.543 ^g	0.609	0.59
c12DCE	$(4.1 \pm 1.7) \times 10^{-5}$	402.3	-1.2	-0.89		0.478	0.564	1.11
t12DCE	$(1.2 \pm 0.4) \times 10^{-4}$		-1.2	-0.85		0.488	0.573	0.80
11DCE	$(6.4 \pm 5.5) \times 10^{-5}$	338	-1.14	-0.72				0.76
VC	$(5 \pm 1.5) \times 10^{-5}$		-0.761	-0.95				1.28
HCA	$(3.1 \pm 3.3) \times 10^{-2}$	288.5	-2.555	0.33		0.66	1.14	0.054
PCA		289.2				0.66	1.05	
1122TeCA	1.3×10^{-2}	315.2	-1.982	-0.34		0.51	0.93	0.51
1112TeCA	1.4×10^{-2}	295.7	-2.39	-0.22		0.56	0.94	0.63
111TCA	1.1×10^{-2}	305.0	-2.16	-0.23		0.57		0.64
12DCA		338.9				0.49	0.73	

Note: a. Jonhson et al. , 1996 ; b. Seetula, J., 1998; Lide, D. R., 2004 ; c. Sherer et al., 1998; d. Sherer et al., 1998; Arnold and Roberts, 1998; e. Vogel et al., 1987; f. Burrow et al., 2000; g. E_1 and E_{2h} values are for transformation from TCE to c12DCE; h. E_{2h} represents E_2 of hydrogenolysis. E_{2r} represents E_2 of reductive elimination.

Since the reduction of HOCs can occur via hydrogenolysis and reductive elimination, different reduction pathways lead to different reduction potentials. Arnold and Roberts (1998) pointed out that separate correlation of hydrogenolysis

rate and reductive elimination rate with E_2 can not only give a good correlation of these parameters but also provide some insight into the distribution of reduction products. They reported that the ratio of reductive elimination to hydrogenolysis increases with the sequence of PCE, TCE to DCE in reaction with zinc.

An interesting observation contradictory to kinetic results shown in Table 2.3 is that some researchers observed that the reactivities of chlorinated ethylenes reduced with the increased degree of chlorination which apparently contradicted the order of the thermodynamic preference of these compounds (Burris et al., 1995; Johnson et al., 1996; Arnold and Roberts, 2000; Farrell et al., 2000; Li, 2002). Farrell et al. (2000) attributed this apparent discrepancy to the different predominant mechanisms for reduction of TCE and PCE. Comparisons of amperometrically measured reaction rates (which represent the direct electron transfer from metal surface to parent compounds) with those measured analytically (which represent sum of direct electron transfer from metal to parent compounds and catalytic hydrodehalogenation reduction with hydrogen as the electron donor) can be used to assess the relative rates of direct and catalytic reductions. It was found that the direct reduction of PCE was 6.8 times faster than the direct reduction of TCE. Thus, the direct reduction rates of TCE and PCE still follow the order of thermodynamic preference of chlorinated ethylenes. However, Farrell et al. (2000) observed that the overall reaction rate constant of TCE was twice as fast as PCE. The discrepancy indicated significantly higher catalytic reduction rate of TCE, compared to that of PCE.

The possibility of higher catalytic reduction rate of TCE is related to the existence of the other oxidant in the system. In the presence of TCE or PCE, Fe oxidation by water accounts for more than 80% of the corrosion (Farrell et al., 2000). Thus, excessive amount of atomic hydrogen are available for catalytic hydrodehalogenation reaction of the substrate in this system. Some researchers (Alonso et al., 2002; Keane et al., 2004) suggested that the catalytic hydrodehalogenation can occur via the electrophilic attack of the dissociated hydrogen on the adsorbed substrate for which the reduction rate will be lower for

the substrate with more electron withdrawing substituents. Thus, due to the existence of the additional electron withdrawing substituents, the catalytic hydrodehalogenation rate will tend to show a lower catalytic hydrodehalogenation rate for the highly chlorinated compounds.

The dominance of the direct reduction process or the catalytic hydrodehalogenation process is related to the pH value of the solution (Wang and Farrell, 2003). Wang and Farrell (2003) indicated that the lower pH value will result in the more importance of the catalytic hydrodehalogenation reaction of TCE. Therefore, they observed that the reduction rate of TCE is higher than that of PCE at pH value of 3.

The surface condition of Fe particles is the second explanation for the similar reduction rate of PCE and TCE (Li, 2002). Usually, the Fe surface will be covered by a layer of oxide film, which acts as a barrier for electron transfer. Therefore, the electrons releasing from Fe surface will be the rate limiting step during the reduction of HOCs. Under the anodic-control condition, the rate of electrons released from iron surface is slow compared to the rate at which electrons are received by oxidant at cathodic site. In this circumstance, the reduction rate is less dependent on the properties of HOCs. Under the cathodic control condition or in the absence of dissolved oxygen, the electron received by the oxidant was the rate limiting step for the whole reduction process. Thus, in this scenario, the reduction rate will reflect the thermodynamic properties of the HOCs.

The last explanation for the discrepancy of the reported reduction rates for PCE and TCE is related to the component of Fe powder. Arnold and Roberts (2000) explained that other researchers, who observed the higher reduction rate of PCE than TCE, used Fe powder with significantly high level of carbon impurities which served as a non-reactive sorptive phase. The adsorption rates for the highly chlorinated ethylenes are usually higher than the lightly chlorinated species (Burris et al., 1995). Therefore, the overall disappearance rate of chlorinated ethylenes, which might incidentally include the reduction of parent compounds and large

amount of sorption to the metal surface, will show the same order as the thermodynamic preference of these species.

2.2.4 Reduction pathways and intermediate byproducts

(a) Chlorinated methanes

The reduction of chlorinated methanes may include sequential and parallel reactions in the degradation of CTC, as described in Fig. 2.6. Matheson and Tratnyek (1994) illustrated that the reduction of chlorinated methanes with ZVI system is mainly through sequential reductive dehalogenation pathway (sequential hydrogenolysis). CTC is first degraded to chloroform (CF), then to methylene chloride (DCM). The reactions become less favorable with each successive dechlorination step. The lower reactivity of DCM results in its accumulation in the aqueous phase.

Fig. 2.6. Proposed reduction pathways of CTC with ZVI (Matheson and Tratnyek, 1994; Balko and Tratnyek, 1998; Lien, 2000; Li, 2002).

In other study, Balko and Tratnyek (1998) indicated that α -elimination is another possible pathway of CTC reduction with ZVI. Dichlorocarbene was reported as the intermediate for α -elimination which could then be hydrolyzed to give carbon monoxide or formic acid (Balko and Tratnyek, 1998; Li, 2002). Many researchers detected methane during reduction of chlorinated methanes (Orth and

Gillham, 1996; Roberts et al., 1996; Fennelly and Roberts, 1998; Lien, 2000). Methane and minor amount of other hydrocarbons were believed to be produced from reduction of carbon dioxide or carbon monoxide through Fischer-Tropsch process (Hardy and Gillham, 1996; Deng et al., 1997; Lien, 2000). This reaction was used in industry to synthesize hydrocarbons with CO and hydrogen in the presence of catalyst, such as Fe, Ni and Co. The key step of Fischer-Tropsch process is the dissociation of adsorbed CO to form surface carbon species. These carbon species then react with the absorbed dissociated hydrogen to form either methane or other hydrocarbons.

Boronina and Klabunde (1995) used various metals, including magnesium (Mg), tin (Sn) and zinc (Zn), to degrade chlorinated methanes. They observed different end products during the CTC reduction with Sn and Zn. The major product was methane in the Zn/water system, or carbon dioxide while in the Sn/water system. It was supposed that the reduction was initiated by formation of organometal intermediate which would then hydrolyze to hydrogenolysis product or decompose to carbene. The competition of hydrogenolysis and elimination pathways led to the formation of different end products.

(b) Chlorinated ethylenes

Compared to the reduction of chlorinated methanes, lower amount of chlorinated intermediate byproducts has been detected during the reduction of chlorinated ethenes (Schreier and Reinhard, 1994; Orth and Gillham, 1996; Arnold and Roberts, 1998, 2000; Farrell et al. 2000; Wang and Farrell, 2003). Ethene and ethane have been confirmed to be the major end products of TCE and PCE reduction.

* R represent Cl for PCE or H for TCE

Fig. 2.7. Hypothesized pathway of PCE or TCE reaction with iron (Orth and Gillham, 1996; Arnold and Roberts, 2000; Wang and Farrell, 2003).

The possible reduction pathways of PCE and TCE are shown in Fig. 2.7. At first a π -bonded surface compound is produced. Orth and Gillham (1996) suggested that the existence of chloroethene-Fe⁰ π bonding is a possible reason to preventing intermediate desorption until the reduction is complete. In the next step, the di- σ -bonded intermediate may reduce through two fast dehalogenation steps to produce an adsorbed double bond intermediate. Then the adsorbed double bond intermediate can undergo further reduction to ethene and ethane, or it may desorb from the iron surface to produce mono- or dichloroacetylene (Wang and Farrell, 2003). The fact that most studies did not observe the chloroacetylenes indicated that further reduction of the adsorbed double bond intermediate byproducts is a more favorable pathway than desorption. Alternatively, the di- σ -bonded intermediates can react with adsorbed hydrogen and then eliminate one chloride ion to form DCEs or TCE

(Arnold and Roberts, 2000). TCE reduction mainly occurs via exclusively indirect degradation by atomic hydrogen at low pH, and via direct electron transfer and catalytic hydrodehalogenation by atomic hydrogen at neutral pH (Wang and Farrell, 2003). In contrast, the reduction of PCE from the di- σ -bonded intermediate to the di- σ -bonded dichloroethylene is through direct electron transfer from Fe to the substrate.

2.2.5 Passive film of ZVI

(a) Air-formed high temperature film

One of the important factors that can influence the reaction rate of Fe is the passive film on the Fe surface. Different kinds of passive films can be formed on Fe surface. The first one is air-formed high-temperature film, and the second kind is solution-formed high-electric field film (Ritter et al., 2002). There is a general agreement that the air-formed high-temperature film is the original air-formed passive film on the iron surface which is composed of mixed Fe_3O_4 (magnetite) and Fe_2O_3 (hematite) (α - and γ - Fe_2O_3) (Balko and Tratnyek, 1998; Adib III et al., 2002). The presence of the air-formed high-temperature film should be expected to reduce the reactivity of the iron (Ritter et al., 2002). Adib III et al. (2002) indicated that α - Fe_2O_3 contains Fe^{3+} in 2/3 of the octahedral interstitial sites within the oxygen lattice of the corundum structure. In the Fe_3O_4 crystal, Fe^{2+} distributed in the octahedral sites and Fe^{3+} distributed equally in the octahedral and tetrahedral sites within the oxygen lattice of its inverse spinel structure. The arrangement of the oxide film always follows two models. In the first model, there are two layers of the film. The outer layer is Fe_2O_3 , and the inner layer is Fe_3O_4 . The other model indicates the existence of Fe^{2+} concentration gradient within the film. The gradient starts at the Fe^{2+} concentration in the inner layer of the Fe_3O_4 film and decreases to that of Fe_2O_3 at outer layer of the film (Balko and Tratnyek, 1998).

Ritter et al. (2002) also pointed out that when exposing Fe coated by Fe_2O_3 to solution, the original oxide film can be removed rapidly from the Fe surface and release Fe^{2+} into solution by autoreduction reaction:

Autoreduction of Fe_2O_3 can also transform Fe_2O_3 to Fe_3O_4 :

Several researchers (Agrawal et al., 2002; Klausen et al., 2003) found that the air-formed oxidation film could dissolve more readily in the presence of dissolved carbonate, because of the formation of stable aqueous complex, such as FeOHCO_3 and $\text{Fe}(\text{CO}_3)_2^-$. However, Balko and Tratnyek (1998) showed that it would take several weeks to convert Fe_2O_3 to Fe_3O_4 and ultimately to green rust. Since their experiments were completed within 3 h, the original oxide film would still remain on the iron surface. Therefore, they concluded that the electron transfer from Fe to parent compounds was through the initial air-formed high-temperature film on the Fe surface. Adib III et al. (2002) observed that CTC can achieve dissociative adsorption in the Fe_3O_4 selvedge of single crystal α - Fe_2O_3 which results in the formation of four desorbing species, including CCl_4 , OCCl_2 , C_2Cl_4 and FeCl_2 . Thus, Fe_3O_4 cannot be considered as a passive film. It can also play a role in the reduction of chlorinated organics (Bonin et al., 1998).

In general, the main roles of oxide film on the Fe surface are (i) acting as electron transfer barrier which makes the reaction taking place mainly at pits and defects; (ii) behaving as a conductor which allows charge to pass through the interface with some resistance; (iii) serving as a catalysis where adsorbed Fe^{2+} can act as a strong reductant (Gaspar et al., 2002); and (iv) restricting hydraulic flow and clogging column system in packed bed reactors or PRBs.

The abundance of non-reactive adsorbates and the presence of passive film act as an additional electron transfer barrier which can reduce the reactivity of iron (Gotpagar et al., 1999). In order to increase reaction rate and to achieve constant initial surface condition, pretreatment of iron powder has been used by many

researchers to reduce the passive film. Acid wash (Matheson and Tratnyek, 1994; Roberts et al., 1996; Arnold and Roberts, 2000; Lin and Lo, 2005) and chloride pretreatment (Gotpagar et al., 1999) are the two widely used methods. Ruiz et al. (2000) observed that sonication of the groundwater-soaked iron could remove the weakly bonded iron hydroxide species and carbonyl-type species, and thus made the surface more reactive. Lin and Lo (2005) also used H₂-reducing process to reduce the residue oxide layer after acid wash process. They indicated that acid washing could increase the surface area of ZVI, but the number of surface reactive sites would decrease due to the rapid corrosion during the rinsing process. The H₂-reducing process may be more effective due to the increase of the amount of reactive site through reducing the passive layer and carbonization of carbon-containing species on the ZVI surface. Therefore, the advantages of pretreatment include: (i) cleaning the oxide film and the impurity, and (ii) increasing the amount of pits and reactive sites.

(b) Solution-formed high-electric field film

Several investigators have observed that the reaction rate for degradation of chlorinated compounds might deviate from the first-order-kinetic model with increasing elapsed time (Wüst et al., 1999). The decreasing reaction rates have been attributed to increasing mass transfer limitations due to the accumulation of the surface oxide layer (solution-formed high-electric film) which changes the reduction from cathodic control to anodic control (Gillham and O'Hannesin, 1994; Farrell et al., 2000). With the disappearance of substrate, Johnson et al. (1998) confirmed the appearance of dissolved Fe²⁺ without colloidal or dissolved Fe³⁺, which indicated the formation of oxidized passive film on the metal surface, such as Fe(OH)₂ and Fe(OH)₃, etc. But the Fe(OH)₂ precipitations are unstable, and will be transformed to Fe₃O₄ and later to Fe₂O₃ (Ritter et al., 2002):

The field and column tests conducted by Farrell et al. (2000) also confirmed this conclusion. Farrell et al. (2000) indicated that the passivating layer on iron filings consisted of an inner layer of Fe_3O_4 with an outer coating of $\gamma\text{-Fe}_2\text{O}_3$. Other kinds of mineral precipitates, including $\beta\text{-FeOOH}$ (akaganeite), $\alpha\text{-FeOOH}$ (goethite) and $\gamma\text{-FeOOH}$ (lepidocrocite), have been found on the surface of permeable iron reactive barriers (Phillips et al., 2003). Fe_2O_3 , as a semiconductor or an insulator, can passivate the metal surface, and hinder the reactions involving the electron transfer. Although Fe_3O_4 is also a semiconductor, the small band gap between its valence bond and conduction bond gives it a better electrical conductivity than Fe_2O_3 .

During the oxidation of $\text{Fe}(\text{OH})_2$, green rust as an intermediate would be produced. O'Loughlin et al. (2003) concluded that the green rust is a mixed ferrous/ferric hydroxides with alternating positively charged hydroxide layers and hydrated anion layers. The general composition is as follow:

where $x = 0.9\text{-}4.2$, A is an n -valent anion (including Cl^- , SO_4^{2-} , CO_3^{2-} , Br^- , I^- , NO_3^- , SO_3^{2-} , etc.) and y is the varying amount of interlayer water ($y = 2\text{-}4$). Green rust compounds are divided into two kinds: green rust one (which includes planar interlayer anions to balance the charge of hydroxide layer, such as $[\text{Fe}_3(\text{II})\text{-Fe}(\text{III})(\text{OH})_8\text{Cl}]$ and $[\text{Fe}_4(\text{III})\text{Fe}_2(\text{II})(\text{OH})_{12}] \cdot [\text{CO}_3 \cdot 2\text{H}_2\text{O}]$) and green rust two (which includes three dimensional anions, such as $[\text{Fe}_4(\text{III})\text{Fe}_2(\text{II})(\text{OH})_{12}] \cdot [\text{SO}_4 \cdot 2\text{H}_2\text{O}]$) (Genin et al., 1998).

Recent research performed by O'Loughlin et al. (2003) suggested that green rust may be a highly reactive reductant in the subsurface environment. However, the reductive transformations of chlorinated hydrocarbons with green rust are typically slower than that with ZVI. They reported that in the presence of transition metal species, such as Ag^{I} , Au^{III} or Cu^{II} , the reduction ability of green rust can be enhanced. The mechanism may be related to the galvanic couple involving green

rust and the transition metals which are reduced to zero-valent forms by the former. Chlorinated compounds can be reduced on the surface of transition metal and the green rust serves as electron donor in this system.

The presence of other ions in the solution can also influence the corrosion of iron. Exposing iron to high concentration of dissolved carbonate species (i.e., $\text{CO}_2(\text{aq})$, $\text{H}_2\text{CO}_3(\text{aq})$, HCO_3^- and CO_3^{2-}) for short time can enhance reduction rate. It was generally assumed that the absorbed H_2CO_3 and HCO_3^- can act as oxidant which will accelerate metal dissolution (Agrawal et al., 2002),

However, for prolonged exposure, the reaction rate would decrease because of the formation of siderite (FeCO_3) precipitation which can reduce porosity and block the access of adsorbate to the reactive site on metal surface.

2.2.6 Nano-scale Fe and bimetallic particle system

Although ZVI technology has been successfully used in the past few years, there still exist the following challenges (Wang and Zhang, 1997; Schrick et al., 2002): (i) the intermediate products produced during the reduction which can be even more toxic than their parent compounds; (ii) the formation of oxide precipitates which can passivate the Fe surface; and (iii) low surface area of Fe, thus large amount of Fe will be needed to achieve acceptable reduction rate for the surface mediated reaction. Usually, reducing the particle size and alloying with another metal are two commonly used approaches to improve the performance of ZVI. Thus, the nano-scale bimetallic particle system has been developed in recent years.

Main advantages of the nano-scale and bimetallic particle system are as follows: (i) higher surface area and density of reactive surface sites, thus less

amount of metal needs to be used to achieve comparable reduction rate as those with larger particles; (ii) catalytic effects of the lower hydrogen over-potential metal which will be effective in catalytic hydrodehalogenation reactions; (iii) the galvanic effects between the two metals, which can inhibit the accumulation of the Fe corrosion products; and (iv) smaller particle size which will provide them more flexibility for in-situ applications such as direct injection of particles (Fig. 2.8) and ex-situ applications in slurry reactor. Due to the advantages of nano-scale bimetallic particles system, considerable efforts have been focused on searching for a more effective and economic catalyst to optimize the system. Usually the reduction rates of HOCs with bimetallic particles are higher than that with ZVI (Wang and Zhang, 1997; Li and Klabunde, 1998; Cheng and Wu, 2000; Kim and Carraway, 2003; Xu et al., 2005^{a, b}). However, Kim and Carraway (2000) reported a slower reduction rate of pentachlorophenol with bimetallic particles compared to that with ZVI. They reasoned that the reactivity of bimetallic particles was directly related to the specific properties of the target compound.

Fig. 2.8. Nano-scale iron particles for in-situ remediation (Zhang, 2003).

(a) *Synthesis of nano-scale bimetallic particles and particle stabilization*

Nano-scale particles have been synthesized by a variety of methods (Wang and Zhang, 1997; Li and Klabunde, 1998; Aiken III and Finke, 1999; Ponder et al., 2001; Schrick et al., 2002; Platt et al., 2003; Chung and Rhee, 2004; Holmberg, 2004; Nurmi et al., 2005; Song and Carraway, 2005), including: (i) wet chemical reduction method, (ii) thermal decomposition or photochemical decomposition of low valent transition metal complex, (iii) metal vapor synthesis, (iv) preparations in micelles and encapsulation, and (v) electrochemical deposition method.

Wet chemical reduction method is commonly applied to synthesize nano-scale particles in the lab-scale experiment. The reductants used in the synthesis include sodium borohydride, sodium citrate, formic acid, hydrazine, etc. A wide variety of zero-valent metals have been prepared with this method, including Fe, Pt, Pd, Ag, Au, etc. For the ZVI system, another catalyst metal can be added to the system to improve the reduction performance. The degree of interaction between the two metals and the distribution of the catalyst component on the Fe surface can influence the catalytic effects (Urbano and Matinas, 2001). Zhang et al. (1998) indicated that physically mixing of Pd and Fe particles produced no positive effects on the TCE dechlorination. A close contact of the Fe with the catalyst metal in bimetallic particles system is essential to obtain a positive effect. Only through coating the catalyst on the Fe surface or forming bimetallic alloy can enhance the reactivity of the system. Synthesis of an alloy or a mixture of two metals may be accomplished through co-reduction method. As an example, nano-scale Ni/Fe particles were synthesized by reducing the solution mixture of ferrous and nickel salts with sodium borohydride solution (Schrick et al., 2002; Wu and Ritchie, 2006). Alternatively, if the nano-scale Fe is to combine with another minor amount of noble metal, such as Pd, Pt and Au etc, post-coating synthesis method should be more suitable (Wang and Zhang, 1997; Zhang et al., 1998; Lin et al., 2004; Xu et al., 2005a). The noble metal will deposit on the surface of nano-scale Fe particles through redox reaction. Usually, the bimetallic particles formed through post-coating method show a distinct core/shell structure (Liu et al., 2005; Nutt et al., 2005). Meanwhile, oxygen atoms are concentrated in the shell of the particles which indicates that the shell is an oxide or oxyhydroxides (Liu et al., 2005). The

advantages of the wet chemical reduction methods are summarized as follows (Kreibig et al., 2001): (i) applicable to most of the transition metals, (ii) narrow particle size distribution, (iii) able to produce nano-scale bimetallic particles easily, and (iv) stable metal colloid and easy to isolate the dry metal particles.

Among all the reductants applied in the wet chemical reduction method, borohydride is one of the widely used species. Ponder et al. (2001) indicated that pH has a strong effect on the size of iron particles formed in borohydride reduction method. The slightly acidic pH of the metal salt solution might be advantage to the formation of smaller nano-scale particles (Wang and Zhang, 1997; Ponder et al., 2001). Besides pH effect, the concentration of the borohydride solution and its rate of addition can also change the composition of the reduction products (Ponder et al., 2001; Holmberg, 2004). The particle size also decreases if the concentration of one reactant is increased far beyond the concentration of the other reactant (Holmberg, 2004).

Borohydride reduction method can result in the surface of the nano-scale Fe enriching in boron (Liu et al., 2005). The main forms and effects of boron on the dehalogenation reactions are still not conclusive. Some researchers indicated that boron may present as a salt on the metal surface or in the bulk in the form of amorphous mixture, which plays a central role in the passive corrosion activities (Ponder et al., 2001, Schrick et al., 2002). Liu et al. (2005) provided another explanation. They indicated that boron would be in the form of Fe-B alloy which would be catalytic species for hydrogenation and catalytic dehalogenation reactions.

Because of the magnetic effects between the smaller particles, the nano-scale particles tend to aggregate into larger particles to achieve thermodynamic minimum. Usually two ways can be used to accomplish the particle stabilization, including electrostatic stabilization and steric stabilization. Electrostatic stabilization is achieved by adsorption of ions to the metal surface which can form electrical double layer to repulse the individual particle. Steric stabilization can be carried out by surrounding the nano-scale metal particle with a layer of sterical bulk

which acts as protective shield. The main protective groups include polymers, copolymers, solvents, surfactants and organometallics.

Other researchers also fixed the synthesized particles on solid surface to give a supported heterogeneous reductant. The solid surfaces served as support for nano-scale particles include silica matrix (Nakagawa et al., 2005), dendrimers (Chung and Rhee, 2003), porous alumina (Platt et al., 2003), hydrophobic resin (Ponder et al., 2001), hydrophilic carbon (Schrack et al., 2002), cellulose acetate (Wu and Ritchie, 2006), etc. Compared to the nano-scale particles without support, supported particles are stable, reusable and easy to separate (Alonso et al., 2002). However, the nano-scale metal particles without supports may also have some advantages (Chung and Rhee, 2003): (i) intrinsic properties of nano-scale particles can be elucidated without the influence of the support, and (ii) the size of particles formed might be more uniform compared to that in the supported system.

(b) Characterization of nano-scale particles

One of the most widely used techniques for characterization of nano-scale particles is transmission electron microscopy (TEM) which can provide morphology, shape and structure of nano-scale particle cluster (Aiken III and Finke, 1999). Nitrogen Brunauer-Emmet-Teller (BET) surface area analysis can show the internal surface area, external surface area and pore size of the particles. The BET surface areas and particle sizes of various nano-scale particles synthesized by the previous researchers are shown in Table 2.4.

X-ray diffraction (XRD) analysis shows the crystal composition of nano-scale particles. It can also indicate the estimated crystal size based on the diffraction width (in radians) at half maximum intensity. Because the size of the nano-scale particles formed is often small, the shape of peak in the XRD patterns is usually broad (Lien, 2000; Schrick, 2002). Schrick (2002) indicated that to gain more information of the nano-scale particles, the particles can be heated in an argon atmosphere to 450 °C, which could sharpen the peaks. Other characterization

techniques, including X-ray absorption near edge spectroscopy (XANES), X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray analysis (EDX), can also be applied to characterize the nano-scale clusters.

Table 2.4 Particle sizes and BET surface areas of various nano-scale particles

Nano-scale Particles (without support)	References	Grain Size (nm)	Surface Area (m ² g ⁻¹)
Precipitate with NaBH ₄	Wang and Zhang, 1997 (Fe or Pd/Fe)	<100	33.5
	Zhang et al., 1998 (Fe or Pd/Fe)	<100	33.9
	Choe et al., 2000; 2001 (Fe)	<100	31.4
	Schrack, 2002 (Fe)	<100	18
	Liu et al., 2005 (Fe)	30-40	36.5
	Schrack et al., 2002 (Ni/Fe)	3-30	59
	Wu and Ritchie, 2006 (Ni/Fe)	11-24	
Reduction of oxidates with H ₂	Nurmi et al., 2005 (Fe)	70	29
	Liu et al., 2005 (Fe)	40-60	23

(c) Reduction products of nano-scale particles

Nano-scale Fe and bimetallic particles, as effective reductants, can reduce a wide variety of environmental contaminants, such as chlorinated aliphatics, chlorinated aromatics and aromatic nitro-compounds (Wang and Zhang, 1997; Zhang et al., 1998; Lien and Zhang, 2001; Choe et al., 2000; 2001; 2004; Schrack et al., 2002; Ghosh et al., 2004; Liu et al., 2005; Song and Carraway, 2005; Wu and Ritchie, 2006). The reductions of these contaminants with nano-scale Fe or bimetallic particles need relatively shorter reaction time and produce less amounts of incomplete reduction byproducts than those with the micro-scale particles. The reaction products of chlorinated ethylenes with nano-scale particles have been identified to be only hydrocarbons, including ethane, ethane, propene, propane, butene and butane (Wang and Zhang, 1997; Zhang et al., 1998; Lien and Zhang, 2001). Under iron limited condition, the commercial nano-scale Fe particles

transform TCE to unsaturated compounds, such as acetylene (84.3 %) and ethene (7.8 %) (Liu et al., 2005). Acetylene, as a reactive intermediate, can be transformed to ethene with excess amount of Fe. Choe et al. (2001) indicated that minor amount of intermediates, such as DCM and 1, 2-dichloroethylene, were also formed during the reduction of CF and TCE with the nano-scale Fe particles, respectively. The yields of methane and ethane for reduction of CF and TCE have been reported as around 70 % and 90 %, respectively (Lien, 2000; Choe et al., 2001; Liu et al., 2005). The synthesis process of nano-scale particles and amount of the particles can also influence the products distribution of chlorinated compounds degradation. Compared to the commercial nano-scale Fe, large amount of H₂ will be evolved with the nano-scale particles which are synthesized with borohydride reduction methods (Liu et al., 2005). The evolved hydrogen gas can be used as reductant for catalytic hydrodehalogenation.

(d) Rate limiting step and dechlorination mechanisms

One criterion to examine the rate limiting step is that the activation energy of surface-reaction process is higher than that of mass-transfer process ($>15 \text{ kJ mol}^{-1}$) (Arnold et al., 1999). Lien (2000) observed that the activation energies for the reduction of PCE with nano-scale Fe and Pd/Fe were 44.9 kJ mol^{-1} and 31.1 kJ mol^{-1} , respectively. It indicates that the surface-reaction process is the rate limiting step in the dechlorination process. The relatively lower activation energy for the reduction of PCE with the bimetallic particles suggests that the existence of catalytic dechlorination reaction in the presence of Pd. The rate limiting step can also be decided by comparing the mass transfer coefficient and the surface reaction rate. With the decrease of particle size from micro-scale to nano-scale, Lien (2000) reported that the mass-transfer rate could be increased by about two-orders of magnitude. Lien (2000) also indicated that the mass transfer rates of trans-DCE with nano-scale particles were so fast that they could be ignored in the consideration of the rate limiting step.

Fig. 2.9. Reduction mechanism of CTC with nano-scale bimetallic particles (Lien, 2000).

The reduction mechanism of CTC with nano-scale bimetallic particles is presented in Fig. 2.9. The tetrahedral structure of chlorinated methanes can not make direct contact of the molecular with the metal surface which leads to the formation of chlorinated intermediates. The main mechanism of methane formation during the CTC reduction was reported to involve surface reactions, due to the less possible of sequential hydrogenolysis reaction (Lien, 2000).

Fig. 2.10. Schematic depiction of PCE with nano-scale Pd/Fe particles (Zhang et al., 1998; Schrick, 2002; Zhang, 2003).

The proposed mechanism of PCE dechlorination with nano-scale Pd/Fe is as shown in Fig. 2.10. The less amount of chlorinated intermediate byproducts observed during the reduction of chlorinated ethylenes may be resulted from the planar structures of this group of compounds which allow full contact of the substrates with the metal surface (Lien, 2000). Song and Carraway (2005) observed that the reductive β -elimination is the major pathway for the dehalogenation of the chlorinated ethanes with α , β -pairs of chlorine atoms, and the reduction rates are higher for the highly chlorinated ethanes. Reductive α -elimination and hydrogenolysis are parallel transformation pathways for compounds with chlorine substitutions on one carbon. The reduction rates are generally higher for the compounds with chlorinated substitutes which are more localized on one carbon (Song and Carraway, 2005).

2.3 Catalytic Hydrodehalogenation

2.3.1 Background

Catalytic hydrodehalogenation is another possible alternative to transform the HOCs contaminants. Heterogeneous catalytic hydrodehalogenation can be carried out in both liquid and gas phases. Mechanisms of the catalytic dehalogenation and the dehalogenation driven by high hydrogen over-potential metal are different. High hydrogen over-potential metal, such as Fe, can act as an electron donor for dehalogenation reaction directly (Kopinke et al., 2004). In the catalytic hydrodehalogenation reactions, catalyst activates the hydrogen atom which can attack the carbon-halogen bond and results in the dehalogenation of the parent compounds. Hydrogen gas and other reductive molecules, such as formic acid, isopropanol, hydrazine and metal hydride, etc., can act as hydrogen donor in this reaction (Kopinke et al., 2004). In general, the use of molecular hydrogen is the most common for the economic convenience of industry application (Urbano and Matinas, 2001). Catalytic hydrodehalogenation mechanisms may include nucleophilic and electrophilic attacks of the dissociated hydrogen on the adsorbed HOCs. The electrophilic mechanism can be diagnosed by increasing reduction rate

with the substituents moving from a strongly electron withdrawing (-Cl) to electron donating (-OH or -CH₃) species (Menini et al., 2000). Many researchers (Menini et al., 2000; Keane et al., 2004) pointed out that the dechlorination rates for chlorinated aromatics followed the sequence chlorobenzene < chlorotoluenes < chlorophenol. This phenomenon indicated the electrophilic mechanism during the dechlorination of chlorinated aromatics.

Although Pd has been proved to be the best choice for dehalogenation among the various kinds of catalysts, many other transition metals, for instance Pt, Ag, Ni etc., can also be effective for catalytic hydrodehalogenation (Heinrichs et al., 1997; Schüth and Reinhard, 1998; McNab et al., 1998; Menini et al., 2000; Bonarowska et al., 2001a, b; Simagina et al., 2003; Keane et al., 2004; Nutt et al., 2005). The catalytic effect of Ni is weaker than Pd, thus the catalytic dehalogenations with Ni usually require severe conditions, such as high temperature and high hydrogen pressure (Simagina et al., 2003). However, its good corrosion stability and lower cost (as compared to Pd) make it appealing for industrial and environmental applications (Menini et al., 2000; Simagina et al., 2003; Keane et al., 2004).

Since heterogeneous catalysis is a surface phenomenon, thus some factors, including particle size, surface area, metal-support interaction and the existence of another metal, will show some influences on the catalytic effects (Alonso et al., 2002). There is no consensus in the structural selectivity of the hydrodehalogenation reaction. Ribeiro et al. (1998) reported that the catalytic dehalogenation was not structural sensitive on Pd surface, and the reduction rate was only related to the total Pd surface area. However, Menini et al. (2000) pointed out that the hydrodechlorination rates and the yield of aromatics were favorable for the larger size of catalyst particles in the supported Ni catalytic system.

Diluting the Pd catalyst with another metal can also change the performance of the single species catalyst (Simagina et al., 2003; Nutt et al., 2005). The performances are directly related to the type of the metal added to the Pd system.

Simagina et al. (2003) indicated that Pd/Ni catalyst was less reactive than the pure Pd for the complete transformation of the chlorinated benzenes to benzene. However, Pd/Au bimetallic particles exhibit a more significant increase in hydrodehalogenation activity than the nano-scale Pd particles, especially for the partly coated Pd/Au particles (Nutt et al., 2005). The increase associated with the Pd/Au particles might be due to the geometrical effects, electronic effects and the existence of Au-Pd active sites.

2.3.2 Kinetics of hydrodehalogenation

(a) Gas phase reactions

In the plug-flow system, under hydrogen rich conditions, the kinetic model can be expressed as (Keane et al., 2004):

$$\ln(1 - x_{Cl})^{-1} = k \left(\frac{W}{F_{Cl}} \right) \quad (2.30)$$

where F_{Cl} is the inlet molar chlorine feed rate (mol h^{-1}), x_{Cl} is the degree of the dechlorination and W is the weight of the catalyst.

(b) Aqueous phase reactions

A Langmuir-Hinshelwood (L-H) formula has been used by Lowry and Reinhard (2001) to express the result of batch system for TCE reduction in the presence of Pd with the hydrogen gas as the reductant. They indicated that the reaction on the surface between the adsorbed H_2 and TCE could be the rate limiting step. The kinetics can be expressed as following equation:

$$\frac{dC}{C_{cat} dt} = -k_{rxn} \left(\frac{K_{TCE} C_{TCE}}{1 + K_{TCE} C_{TCE}} \right) \left(\frac{K_{H_2}^n C_{H_2}^n}{1 + K_{H_2}^n C_{H_2}^n} \right) \quad (2.31)$$

where k_{rxn} is the apparent rate constant; C_{cat} is the catalyst concentration; K_{TCE} and K_{H_2} are the Langmuir adsorption constant; C_{TCE} and C_{H_2} are aqueous concentration of TCE and H_2 respectively, n equals to 0.5 for dissociative adsorption of H_2 and equal to 1 for molecular adsorption of H_2 . Usually the coefficient n is fixed at 0.5. At a constant H_2 concentration the decay of TCE has been reported to follow first order kinetics for an initial concentration of TCE as high as 250 μM (Lowry and Reinhard, 1999; 2001). Thus, Eq. 2.31 can be simplified to a first-order model:

$$\frac{dC}{C_{\text{cat}} \cdot dt} = -k_{\text{obs}} \cdot C_{\text{TCE}} \quad (2.32a)$$

$$\text{where} \quad k_{\text{obs}} = k_{\text{rxn}} K_{\text{TCE}} \left(\frac{K_{\text{H}_2}^n \cdot C_{\text{H}_2}^n}{1 + K_{\text{H}_2}^n \cdot C_{\text{H}_2}^n} \right) \quad (2.32b)$$

According to Lowry and Reinhard (1999; 2001), the TCE degradation rate tends to increase with increasing aqueous-phase H_2 concentration ($[\text{H}_2]_{\text{(aq)}}$). The reactions approaches zero-order slowly with respect to the $[\text{H}_2]_{\text{(aq)}}$. They reported that when $[\text{H}_2]_{\text{(aq)}}$ is over 1000 μM , the apparent increase in the $[\text{H}_2]_{\text{(aq)}}$ concentration only gave moderate increase in the TCE reaction rate (Lowry and Reinhard, 2001).

To simplify the calculation process, first-order kinetic model has been widely used by many researchers in the catalytic hydrodehalogenation reactions (Siantar et al., 1996; Lowry and Reinhard, 1999; Zinovyev et al., 2002; Keane et al., 2004; Kopinke et al., 2004; Nutt et al., 2005):

$$\frac{dC}{dt} = -k_{1,\text{obs}} C \quad (2.33)$$

where C is the substrate concentration and $k_{1,\text{obs}}$ is the observed first-order rate constant. If catalyst is on porous supports, the reduction rate of parent compound

may be controlled by mass transfer step. Thus, the kinetic model is zero-order (Siantar et al., 1996):

$$\frac{dC}{dt} = -k_{0,obs} \quad (2.34)$$

where $k_{0,obs}$ is the observed zero-order rate constant.

For the heterogeneous reaction in the constant volume batch reaction system, the kinetic equation with shifting order from zeroth to first with respect to the reduction of parent compounds has also been proposed (Schüth and Reinhard, 1998):

$$\frac{dC}{dt} = -\frac{k_1 C}{1 + k_2 C} \quad (2.35)$$

where k_1 and k_2 are the constants. If the reaction is reversible, the combined zero- and first-order kinetic model can be developed into the following equation (Schüth and Reinhard, 1998):

$$\frac{dC}{dt} = \frac{k_1 (C - C_{eq})}{1 + k_2 C} \quad (2.36)$$

where C_{eq} is the parent compound concentration at reaction equilibrium.

Some researchers reported that the reduction of chlorinated methanes showed the trend which was consistent with the thermodynamic data of these compounds in which their reduction rates tend to increase with the increasing degrees of chlorination (Lowry and Reinhard, 1999). However, other researchers (Schüth and Reinhard, 1998; Alonso et al., 2002; Zinovyev et al., 2002; Keane et al., 2004) also found opposite sequence which indicated the increasing dehalogenation rates with the decreasing degree of halogenation for chlorinated

ethenes and chlorinated aromatic compounds in the presence of the supported Pd. Keane et al. (2004) attributed this phenomenon to the electrophilic mechanism during the reduction of the unsaturated chlorinated compounds. The existence of the second electron withdrawing chlorine on the benzene or ethylene reduced the electron density associated with the carbon ring or the carbon double bond which deactivated the dechlorination process. Some researchers also observed the lower hydrodehalogenation rate of bromobenzene compared to that of chlorobenzene (Menini et al., 2000). This sequence is against the relative bond strengths of this group of compounds. The possible explanation is a less effective activation of C-Br bond for attack by hydrogen.

2.3.3 Reduction products and pathways

(a) Halogenated methanes

Lowry and Reinhard (1999) reported that the primary reduction product of CTC and CF with Pd catalyst is methane. Except CF, other chlorinated methanes were not detected by them during the CTC reduction. Trace amount of DCM was observed in the CF reduction system. In the presence of Pd catalyst, they observed that DCM did not show apparent reduction. Their proposed dechlorination pathways of CTC with Pd are shown in Fig. 2.11.

Fig. 2.11. Proposed catalytic dechlorination pathways of CTC (Lowry and Reinhard, 1999).

Bonarowska et al. (2001a,b) studied gas phase reduction of dichlorodifluoromethane (CCl_2F_2) with Pd, and found that difluoromethane and methane were the two main products. With addition of Au, the selectivity for difluoromethane increased to over 90%. Bonarowska et al. (2001a) indicated that with 20% of Au was sufficient to increase the selectivity for difluoromethane to over 90%. Further increasing Au content only resulted in the sharp decrease of the overall conversion. The high selectivity of difluoromethane was believed to be related to the weak adsorption of CF_2 species on the mixed Pd-Au. The adsorbed carbene species can be formed by two sequential dechlorination steps (Urbano and Marinas, 2001). Deshmukh and d'Itri (1998) reported direct evidence for the existence of metal-carbene species with Pd as the catalyst. They also indicated that the parallel pathways after the formation of difluorocarbene species can result in the formation of methane and difluoromethane. The reduction pathways of dichlorodifluoromethane with Pd are shown in the following figure. The observation of coupling product, ethane, indicated the existence of carbene ($:\text{CH}_2$) species. However, the formation of fluorocarbene coupling products is directly related to the catalyst type. Pd metal or Pd-Au bimetals is usually unselective to fluorocarbene coupling species (Deshmukh and d'Itri, 1998; Bonarowska et al., 2001a,b). Previous studies have found that addition of Fe or Co to the Pd catalyst led to the formation of significant amount of fluorinated dimerization products (Coq et al., 1993; Deshmukh and d'Itri, 1998).

Fig. 2.12. Reduction pathways of CCl_2F_2 with Pd (Deshmukh and d'Itri, 1998).

(b) Halogenated ethylenes

In the presence of Pd and hydrogen gas, the chlorinated ethylenes in the aqueous phase may undergo hydrodehalogenation and hydrogenation of double bond to produce ethane as well as minor amount of ethene in the aqueous phase reaction (Schreier and Reinhard, 1995; Lowry and Reinhard, 1999). In the hydrogen rich conditions, the primary reduction product of PCE and TCE was ethane with trace amount of transient chlorinated intermediates (Schreier and Reinhard, 1995; Lowry and Reinhard, 1999; 2001; Nutt et al., 2005). Lowry and Reinhard (2001) reasoned that the insignificant formation of other chlorinated intermediates indicated the direct transformation of chlorinated ethylenes to ethane.

In the hydrogen limited conditions, Lowry and Reinhard (2001) reported that the maximum amount of chlorinated intermediate products increased with the decrease of the aqueous-phase H_2 concentration ($[H_2]_{(aq)}$). However, the product distribution of intermediates did not show much dependence on $[H_2]_{(aq)}$. Minor amounts of dimerization hydrocarbons, including 1-butene, butane and 2-hexene, etc., were also observed during the reduction of TCE. The total amount of dimerization products increased with the decrease of $[H_2]_{(aq)}$. Meanwhile, when the $[H_2]_{(aq)}$ was lower than 100 μM , the reaction shifted to tending to form unsaturated product.

Nutt et al. (2005) conducted that in the Pd/Au bimetallic particle system, the reduction products were directly related to the Pd coverage. When the Pd coverage was higher than one monolayer, the primary product of TCE reduction was ethane. The performance of these bimetallic particles was similar to the pure Pd catalyst. However, with the low Pd coverage, the primary product shifted to ethene. Based on this phenomenon, they proposed that the adsorbed chlorinated ethylenes were dechlorinated to ethene which was then further reduced through hydrogenation process to ethane. Heinrichs et al. (1997) also observed that the dilution of Pd with an inert metal Ag can lead to the reduction product of dichloroethane from saturated product ethane to unsaturated ethylene in the gas phase reaction. Sinfelt (1983)

believed that the selectivity might be due to the formation of ethane that required larger surface sites than that of ethene. However, Heinrichs et al. (1997) explained that although Ag could react with chloride to form AgCl, it could not hold the rest of the molecular ($\cdot\text{CH}_2 - \text{CH}_2\cdot$) firmly. Thus, the release of the fragment ($\cdot\text{CH}_2 - \text{CH}_2\cdot$) resulted in the formation of ethylene. Ag alone was not reactive because of the quick deactivation by AgCl formed. Once it was combined with Pd, the deactivated part could be reduced by the hydrogen atoms which were adsorbed by Pd. The hydrogen rich surface condition of Pd could also lead to the quick reduction of ethylene to ethane.

2.3.4 Catalyst deactivation

The main problem associated with catalytic dehalogenation is catalyst deactivation. Usually, there are four reasons leading to the deactivation (Lowry and Reinhard, 2000; Menini et al., 2000; Bonarowska et al., 2001^a; Urbano and Marinas, 2001; Simagina et al., 2003): (i) inhibiting effect of hydrogen halides; (ii) formation of the carbonaceous deposits; (iii) sintering of the active metal; and (iv) the catalyst deactivation and degradation in the corrosive environment. The influences of the particle size on the catalyst resistance to the deactivation are not coincident. Menini et al. (2000) indicated that the large Ni particles may be more prone to coking. Other researchers observed a contradictory result which indicated a better resistance to the catalyst deactivation with the bigger catalyst particles (Coq et al., 1986; Aramendia et al., 1999; Urbano and Marinas, 2001). Poisoning effect of hydrogen halide is common for the gas-phase process and in the aqueous phase batch reaction system, and it can be controlled by adding a base compound, such as ammonium hydroxide, sodium hydroxide, sodium acetate, etc., to the reaction medium.

CHAPTER 3.

Transformation of Chlorinated Methanes by Nano-scale Fe and Ni/Fe Particles

3.1 Introduction

Chlorinated organic compounds (COCs), including carbon tetrachloride (CTC) and chloroform (CF), are among the most undesirable compounds in industrial effluents due to their persistence and toxicity. Many of these compounds are known or suspected carcinogens and mutagens. Due to their accidental spills, leakages and improper disposals, these compounds have been continuously released into soil and natural water bodies. Currently, the most common treatment methods for COC-contaminated waters involve phase transfer process such as adsorption by activated carbon and air stripping. Although phase transfer methods are effective in removing these COCs from the aqueous phase, they transfer the contaminants to another medium which still needs further treatment. On the other hand, biotransformation of COCs is a rather slow process as many COCs are recalcitrant. In recent years, there has been increasing interest in developing abiotic reductive transformation method to transform COCs into non-toxic or biodegradable compounds. Reductive elimination of COCs with zero-valent Fe (ZVI) is one

promising method and it has been used in permeable reactive barriers for in-situ treatment of COCs-contaminated groundwater.

The reductive transformation of COCs by various zero-valent metals have been studied by many researchers (Matheson and Tratnyek, 1994; Schreier and Reinhard, 1994; Johnson et al., 1996; Roberts et al., 1996; Arnold and Roberts, 1998; 2000; Choe et al., 2001; Morales et al., 2002; Clark II et al., 2003). Gillham and O'Hannesin (1994) concluded that reduction of halogenated compounds by ZVI is abiotic, heterogeneous, and electrochemical reaction in which Fe is oxidized and the halogenated compounds are reduced. ZVI is one of reductants in the water/Fe system, and there still exist other reducing agents such as Fe^{2+} and H_2 which are produced from the corrosion of Fe particles in water. Matheson and Tratnyek (1994) also indicated that the reduction of chlorinated methanes with ZVI includes direct electron transfer from Fe surface to substrates and indirect electron transfer from Fe^{2+} and H_2 .

Matheson and Tratnyek (1994) illustrated that reduction pathway for chlorinated methanes in the Fe- H_2O system followed sequential reductive dehalogenation. CTC was first reduced to CF, then to dichloromethane (DCM). Consequently, the DCM produced would accumulate in the aqueous system due to its low reduction rate. Boronina and Klabunde (1995) observed that the major product during the reduction of CTC with Zn was methane, while the reduction product of CTC with tin (Sn) was CO_2 .

The reduction of chlorinated methanes has been generally assumed to follow a pseudo-first-order kinetic with respect to the decay of parent compound (Matheson and Tratnyek, 1994; Gillham and O'Hannesin, 1994; Burrow et al., 2000; Clark II et al., 2003). Since the reaction takes place on the surface of Fe particles, a linear relationship has also been observed between the observed rate constant and the available surface area of metal (Johnson et al., 1996; Wüst et al., 1999). The reactivity of COCs with Fe usually reduces with the decreased degree of

chlorination (Matheson and Tratnyek, 1994; Johnson et al., 1996; Scherer et al., 1998; Schrick et al. 2002; Janda et al., 2004).

Although zero-valent Fe has been successfully used in the past few years in treating COC-contaminated waters, there still exist some challenges to apply this technique such as: (i) the intermediate chlorinated byproducts produced during the reduction can be even more toxic than their parent compounds; (ii) the reduction rate will decrease with increased elapse time due to the formation of oxide layers that can block the Fe surface active sites; and (iii) the reductive dechlorination rates of contaminants can be low, thus a long reaction time is needed for complete reduction of the target compounds.

To overcome these problems, treatment technology with bimetallic particles has been developed. Cheng and Wu (2000) observed that combination of Zn or Fe with Ni or Pd indeed had strong promotional effects on the reduction reaction of TCE. Clark II et al. (2003) found that Ni-plated Fe was more effective than the acid-pretreated Fe and the untreated Fe in PCE degradation. Wang et al. (2004) illustrated that Ni appeared to be catalytic in promoting methane production over CF during the reduction of CTC. Although several researchers found that the palladized Fe was very effective in reductive dechlorination of COCs (Muftikian et al., 1995; Korte et al., 2000; Cheng and Wu, 2000), the use of Pd, a precious metal, was less economically viable compared to Ni. Beside bimetallics involving Fe, other bimetallic particles, such as Pd/Mg, Pd/Zn, etc., were also synthesized and found effective in degrading persistent COCs (Li and Klabunde, 1998; Engelmann et al., 2001; Lien and Zhang, 2002).

To date, nano-scale bimetallic particle technology has been proved to be a possible solution to removing COCs. However mechanistic study of COCs transformation with nano-scale bimetallic particles remains limited. The main objectives in this chapter are: (i) to develop suitable method to synthesis nano-scale Fe and bimetallic particles; (ii) to obtain the morphologies of the lab-synthesized nano-scale particles; (iii) to investigate the reduction properties of the particles with

CTC and CF as the target compounds; and (iv) to propose the possible reduction pathway of chlorinated methane with the nano-scale particles.

3.2 Materials and Methods

3.2.1 Chemicals

All aqueous solutions were prepared with ultra-pure water (18.2 MΩ cm). The following chemicals were used as received without further purification: CTC (BDH, UK), CF (Fisher Scientific, NJ), DCM (J. T. Baker, NJ), Fe powder (99.6%, J. T. Baker, NJ), Zn powder (Wako, Japan), ferrous sulfate (FeSO₄·7H₂O) (Reachim, Russia), nickel dichloride (NiCl₂·6H₂O) (BDH, UK), methanol (J. T. Baker, NJ), acetone (Merck, Germany), hexane (Merck, Germany), mercuric thiocyanate (Hg(SCN)₂) (Merck, Germany), ferric nitrate (Fe(NO₃)₃·9H₂O) (Sigma-Aldrich, USA), sodium chloride (Lancaster, UK), sodium hydroxide (Lancaster, UK), methane (5%, National Oxygen Pte Ltd, Singapore).

3.2.2. Preparation of metal particles

Synthesis of the nano-scale Ni/Fe particles was carried out by using sodium borohydride (NaBH₄) as the reductant. The process is depicted in the following equation:

In all synthesis, 12.3 g FeSO₄·7H₂O and 3 g NiCl₂·6H₂O were dissolved in 600 ml ultra-pure water (18.2 MΩ cm) with continuous shaking at 120 rpm, resulting in solution pH in the range of 3.3 to 4.0. The desired ratio of Ni to Fe in the synthesized nano-scale Ni/Fe particles was 1:4 (w/w). NaBH₄ solution was prepared by dissolving 6 g NaBH₄ in 400 ml ultra-pure water. After adding the NaBH₄ solution drop-wise into the Ni/Fe solution, black particles formed. The mixture was then shaken for another 20 min. The particles were then isolated by vacuum

filtration through 0.2 μm cellulose acetate membrane filter. To get rid of the excess borohydride, the particles were washed with 100 ml of ultra-pure water for 3 times and then rinsed with 20 ml of acetone. At last the Ni/Fe particles were dried in freeze drier over night to avoid unexpected oxidation. Similar synthesis and preservation methods were also adopted for synthesis of the nano-scale Fe by adding NaBH_4 solution to $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution.

In the preliminary dechlorination experiment with the commercial Fe powder, it was observed that the reduction rate was extremely low at the initial 16 h. The delay of the dechlorination reaction was related to the oxidation occurred to the commercial Fe. Thus, in order to remove the passive film on the surface of commercial Fe powder, these particles were washed with 1 M HCl once and then rinsed with ultra-pure water for three times. At last, they were dried in freeze drier over night before use. The commercial Zn powder was used directly without further purification and acid pretreatment.

3.2.3. Characterization of particles

Brunauer-Emmett-Teller (BET) surface area analysis of the synthesized nano-scale particles and commercial micro-scale Fe and Zn was performed using nitrogen adsorption method with Quanta Chrome autosorb automated gas sorption system. The surface elemental composition of the nano-scale particles was analyzed with scanning electron microscope (SEM, JSM-6360) combined with energy-dispersive X-ray spectrometry (EDX, JED-2003 X-ray analyzer).

X-ray diffraction (XRD) analysis of mineralogical characteristics of the nano-scale particles was carried out using Bruker D8 advanced XRD diffractometer at 40 kV and 40 mA. Copper metal radiation was used to produce X-rays ($\lambda = 1.5418 \text{ \AA}$). Particle samples were placed into plastic holder, and the scan rate was set at 2θ of 0.75 degree per min. Scherrer Equation (Cullity, 1978) can be used to estimate the crystal size of the nano-scale particles from their XRD pattern:

$$t = \frac{0.9\lambda}{B \cos \theta} \quad (3.2)$$

where t is the median crystal size, B is the full width in radians at half maximum intensity, λ is the x-ray wavelength and θ is the angle at the maximum intensity. To get the images of the structures and sizes of the nano-scale particles, transmission electron microscope (TEM) images were obtained with JEOL electron microscope (JEM-2010) operated at an acceleration voltage of 300 kV. For the commercial micro-scale Fe and Zn, their particle sizes of the commercial micro-scale Fe and Zn were measured by Mastersizer (Malvern).

3.2.4. Experimental system

Batch reduction experiments without headspace were carried out in 40-ml TFE-sealed screw cap bottles covered with aluminum foil. A volume of 40 ml ultra-pure water at pH 7.0 was added to each bottle so that no head-space was left. Reactions with the nano-Ni/Fe particles were studied using a metal loading of 2.5 g l^{-1} , while reactions with the commercial Fe and Zn powder were studied using 125 g l^{-1} . The higher loading of the commercial metal particles than the nano-scale particles in the batch experiments was to achieve a comparable total metal surface area concentration in the solution ($\text{m}^2 \text{l}^{-1}$). CTC and CF were introduced to the system via a methanolic spike resulting in about 0.3% methanol by volume. Reactions were preformed at initial concentrations of 130 μM for CTC and 165 μM for CF in single species system.

In the preliminary experiment, the pH of the solution was measured in the aqueous sample. It was found that the pH values generally hovered at around 8, indicating mild pH increase only during the experiment. Due to the insignificant pH change, pH buffer was not added to control the pH value in the aqueous phase.

The filled bottles were placed on an orbital shaker (300 rpm) at room temperature ($22 \pm 1^\circ\text{C}$). At each predetermined reaction time, the scarified bottle

would be taken out and analyzed for chlorinated methanes and chloride ion released. For each sacrificed bottle, 5 ml of aqueous solution was withdrawn at a specific time by a gas-tight syringe with a 0.45 μ M nylon syringe filter for analysis of the concentration of parent compound and its byproducts using gas chromatograph (GC). The preliminary assessment on the nylon filters showed that they were not adsorptive for the halogenated methanes. Another 5 ml of solution was withdrawn for analysis of the concentration of dissolved chloride anion using Flow Injection Analyzer with Ion Chromatograph (FIA/IC, Lachat, QuickChem 8000). After withdrawing the aqueous samples, 10 ml headspace would be left in each bottle. To measure the evolved methane, 200 μ l of headspace was withdrawn with gas tight syringe and injected into another GC directly. The methane concentrations were measured in percentage in the gas phase. Based on the Henry's Law, the methane concentration in the aqueous phase of the non-head space system could be calculated. The dissolved Fe, Ni and Zn cations were also analyzed using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Perkin-Elmer, Optima 2000DV).

In analysis of chlorinated methanes, the 5-ml aqueous sample was injected into purge & trap (Tekmar Dohrmann solatek 72 multi-matrix vial autosampler & 3100 sample concentrator) and then analyzed by GC (HP5890) with a HP-5-mega column (30 m-long $\times$ 0.53 mm-ID with 1.5 μ m film thickness) and flame ionization detector (FID). Temperature conditions of GC were programmed as follows: oven temperature at 35 $^{\circ}$ C for 4 min and then increased to 150 $^{\circ}$ C for 1 min at the rate of 6 $^{\circ}$ C per min, injector port temperature at 200 $^{\circ}$ C, and detector temperature at 250 $^{\circ}$ C. Methane was analyzed with GC/FID with a J&W scientific GS-Alumina column (50 m-long $\times$ 0.53 mm-ID). The temperature programs were as follows: oven temperature at 150 $^{\circ}$ C, and both injector port and detector temperature at 200 $^{\circ}$ C.

In order to detect hydrogen gas, other chlorinated intermediate byproducts, and hydrocarbon products which were emitted into air phase during the reduction reaction, batch reduction experiments were repeated using 60-ml serum bottles so that 20 ml of head space was left in each bottle. Other experimental conditions

remained the same as before. At each specific time interval, one of the bottles was sacrificed and its 200 μl gas of the headspace was withdrawn with 250 μl gas syringe and directly injected into GC/MS (Agilent 6890 Series GC, 5973 Network Mass Selective Detector) with DB-5 column (30 m-long $\times$ 0.53 mm-ID with 1.5 μm film thickness) for analysis of the reaction byproducts. Oven temperature, detection temperature and injection temperature were set at 75 $^{\circ}\text{C}$, 280 $^{\circ}\text{C}$ and 280 $^{\circ}\text{C}$, respectively. Meanwhile, hydrogen was analyzed with a GC (HP5890) equipped with a Hayesep Q column (6FT $\times$ 1/8 in $\times$ 2.11 mm) and thermal conductivity detector. Argon was used as the carrier gas. Oven temperature, injection temperature and detection temperature were set at 50 $^{\circ}\text{C}$, 100 $^{\circ}\text{C}$ and 200 $^{\circ}\text{C}$, respectively.

3.3 Results and Discussions

3.3.1. Properties of metal particles

Figure 3.1 shows the SEM images, EDX spectrum and elemental map of the fresh lab-synthesized nano-scale Ni/Fe particles. Ni and Fe were observed to distribute evenly on the surface of particles (Figs. 3.1c and d). Small amount of oxygen was also detected on the surface of the nano-scale particles. The EDX elemental map of fresh nano-scale Fe (figure not shown) has similar pattern as that of Ni/Fe particles, except that Ni was not found in the elemental map and the EDX spectrum.

Fig. 3.1. SEM images, EDX spectrum and elemental map of fresh nano-scale Ni/Fe: (a) SEM image of Ni/Fe particles; (b) EDX spectrum ; (c) elemental map of Fe for Ni/Fe particles; (d) elemental map of Ni for Ni/Fe particles.

Figure 3.2 presents the TEM images of the lab-synthesized nano-scale Ni/Fe and nano-scale Fe particles. The diameters of the nano-scale Ni/Fe and Fe particles were generally smaller than 50 nm and 100 nm, respectively. The particles tended to aggregate together to form chain structures which have resulted from the magnetic interaction.

Fig.3.2. Transmission electron microscope (TEM) images of: (a) nano-scale Ni/Fe particles and (b) nano-scale Fe particles.

The XRD patterns of the nano-scale Fe and Ni/Fe particles are shown in Fig. 3.3. The peaks identified on the XRD patterns were confirmed to be associated with body-centered cubic (bcc) iron. Oxidized forms, such as Fe_2O_3 and Fe_3O_4 , etc., which might exist as small amount of surface coating, could not be detected from the XRD patterns. The wider peak in the Fig. 3.3b indicated that the crystal size of the nano-scale Ni/Fe particles was smaller than that of the nano-scale Fe. Usually the lattice structure of pure Ni was face-centered cubic (fcc), but the diffraction peaks of fcc were not observed. Since the Ni/Fe particles were synthesized from the nickel and ferrous solution mixture, it was believed that alloy Ni/Fe particles were produced during the co-reduction process. The XRD patterns of Ni/Fe particles indicated that Ni atoms were completely incorporated in the bcc Fe lattice. Thus, the lattice spacing of the nano-scale Fe and Ni/Fe was calculated to be $2.86\text{\AA}$ (using Bragg equation).

Fig.3.3. XRD patterns of: (a) nano-scale Fe particles, and (b) nano-scale Ni/Fe particles.

Table 3.1 compares diameters and BET surface areas of the lab-synthesized nano-scale particles and the commercial micro-scale metal particles. The nano-scale particles had BET surface areas of one to two orders of magnitude higher than those of commercial metal particles. The BET surface area of the nano-scale Ni/Fe particles was 1.5 times of the nano-scale Fe, which also indicated the bigger particle size of the latter compared to the former.

Table 3.1 Diameters and BET surface areas of various metal particles

Particles	Grain Size	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Density (kg m^{-3})
Nano-scale Ni/Fe (1:4)	<50 nm ^a	39.17	8020
Nano-scale Fe	<100 nm ^a	26.45	7800
Commercial Fe (Baker)	28.29 μm^b	1.32	7800
Commercial Zn (Osaka)	10.55 μm^b	0.401	7140

Note: a. determined from TEM images

b. measured with Mastersizer (the grain size was represented by D50)

3.3.2. Transformation of chlorinated methanes

(a) Nano-scale Ni/Fe particles

Figure 3.4 presents experimental results as well as simulated curves (which will be discussed in Section 3.4.4) for the CTC reaction with the nano-scale Ni/Fe particles. CTC was degraded to below GC detection limit ($<50 \mu\text{g l}^{-1}$) within 20 min or equivalent to a half-life of shorter than 5 min. CF was the main detected reactive intermediate. Its concentration reached a peak at 20 min and then reduced to below $8 \mu\text{M}$ (6%) after 3 h. Concomitant to the degradation of CTC and CF, the concentration of DCM increased steadily from $0.5 \mu\text{M}$ to $15 \mu\text{M}$. No apparent reduction of DCM was observed during the 3-h reaction. The yield of DCM was lower than 12%. Methane was identified as the main non-chlorinated product in the headspace indicating that it was the major persistent end product of CTC reduction. Trace amounts of other hydrocarbons, such as ethane, ethane, butane etc., were also observed in the system. An increasing chloride concentration was detected in the aqueous phase as the reduction reaction proceeded. Mass balance of the system could be assessed on the basis of the total chlorine mass and total carbon concentration in the system. The total chlorine mass calculated as sum of chloride ion and chlorine in the chlorinated methanes detected at various reaction times ranged from 88% to 103% of the initial chlorine mass. The sum of methane and chlorinated methanes at the end of the experiment was 90% of the initial value. The

reasonably good mass balances achieved in the aqueous phase throughout the experiment indicated insignificant leakage, adsorption of chlorinated methanes to glass wall, or formation of other COCs and hydrocarbons during the experiment. Besides CF and DCM, PCE was also found as one of the other intermediate byproducts detected in the aqueous phase, but its concentration was around or below its GC detection limit. An increased pressure in each bottle was also observed during the batch reduction experiment. The high pressure was resulted from the evolution of H_2 and the production of methane.

Fig. 3.4. The experimental results and simulation curves for reduction of CTC with nano-scale Ni /Fe.

Compared with CTC, CF had a slower reaction rate as shown in Fig. 3.5. The concentration of CF was reduced to below 1% of its initial concentration only after 10 h. The appearance of DCM accounted for 20% of the CF lost. Methane was observed in the gas phase, which accounted for over 70% of CTC lost. The increased quantity of chloride ion in excess of the amount estimated from CF transformation to DCM also confirmed the production of non-chlorinated products. Approximately 91% of chlorine mass balance was achieved at the end of this experiment. Trace amount of PCE was also detected in the aqueous phase.

Fig. 3.5. The experimental results and simulation curves for reduction of CF with nano-scale Ni/Fe.

(b) Nano-scale Fe particles

Figure 3.6a depicts experimental results of CTC reduction with 2.5 g l^{-1} nano-scale Fe particles obtained within the first 2 h of the 95-h experiment. The reduction rate was slightly lower than that with the Ni/Fe bimetallic particles. Transformation of CTC to lower than 1% of its initial concentration was achieved within 1 h. The CF concentration reached a maximum (81%) at around 1 h, and decreased thereafter. The maximum yield of CF was higher than that produced by the nano-scale Ni/Fe particles. Measurements at longer reaction duration (Fig. 3.6b) indicated that CF was subsequently degraded to below 5% at 95 h while the ultimate yield of DCM was 27% (36 μM). Methane was also detected as the main non-chlorinated product.

If the reaction were extended to beyond 10 h, the concentration of methane formed was lower than the prediction value, as shown in Fig. 3.6b. The calculated sum of concentrations of chlorinated methanes and methane was only 65% of the initial CTC concentration. However, the mass balance calculated based on total chlorine was over 90% of its initial mass at the end of the experiment. The good total chlorine mass achieved in the system reflected the insignificant adsorption and

mass loss of methane and chlorinated methanes, or formation of other chlorinated compounds. The discrepancy between the chlorine mass balance and carbon mass balance indicated the formation of other hydrocarbons as the byproducts during the CTC reduction. Based on the GC/MS analysis, various hydrocarbons, such as ethane, ethene, and butane etc., were observed in the aqueous and gas phase, including some long-chain hydrocarbons. However, their amounts were usually around detection limits.

Fig. 3.6. The experimental results and simulation curves for reduction of CTC with nano-scale Fe: (a) up to 2 h; (b) up to 95 h.

In the CF reduction experiment with the nano-scale Fe, it took around 95 h to reduce CF from its initial concentration of 165 μM to 5 μM (3.5%) (as shown in Fig. 3.7). The yield of DCM was 41% (67.8 μM) at 95 h. The reduction rate of CF with the nano-scale Fe particles was apparently lower than that with the nano-scale Ni/Fe particles. Discrepancy in methane yield was also observed in the reduction of

CF with zero-valent Fe, because other hydrocarbons were also found in the gas and aqueous phases.

Fig. 3.7. The experimental results and simulation curves for reduction of CF with nano-scale Fe.

(c) Commercial Fe powder

The experimental results of reaction of CTC with the commercial Fe powder are shown in Fig. 3.8. Complete reduction of CTC could only be achieved after 4 h. CF produced reached its peak concentration (74%) at around 4 h and then began to decrease, while the concentration of DCM increased concomitantly with the reduction of CTC. The final yield of DCM was around 22% (28.8 μM). DCM, as a main chlorinated byproduct, could not endure further reduction. It would accumulate in the aqueous phase. In the CF reduction experiment, it took over 50 h for CF concentration to reduce to 8% of its initial concentration (as shown in Fig. 3.9). Methane was also the main non-chlorinated product detected.

Fig. 3.8. The experimental results and simulation curves for reduction of CTC with Fe powder.

Fig. 3.9. The experimental results and simulation curves for reduction of CF with Fe powder.

Pretreatment of the commercial Fe powder was an important process for the kinetic observation. Due to long period of storage, the surface of Fe powder would be covered by a discontinuous passive oxide film (i.e., Fe_2O_3 , etc.) which resulted in the slower reduction rate at the initial stage (around the first 16 h) (figure not shown). However, it was observed that the reactivity of the commercial Fe powder was revitalized after that, and the COCs reduction with the commercial Fe still followed the pseudo-first order kinetics. Apparently, when exposing the oxide film

to the solution, the film could be removed through the auto-reduction reaction (Balko and Tratnyek, 1998; Ritter et al., 2002), as depicted by the following equation:

(d) Commercial Zn powder

Figure 3.10 illustrates the results of CTC reduction with the commercial Zn powder. The figure shows that 130 μM of CTC was completely degraded within 1.5 h. The concentration of CF reached a peak level (63%) at 1 h and then disappeared after 6 h. The concentration of the DCM produced increased steadily with the progress of CTC and CF reductions, indicating its continual accumulation in the aqueous phase. Around 84% CTC was transformed into DCM over 6 h. No apparent further reduction of DCM to methane was observed at the extended period of this experiment. This finding is further evidenced in Fig. 3.11, which shows that the amount of DCM produced corresponded reasonably well to the amount of CF degraded by Zn, and the DCM produced persisted beyond 10 of reaction.

Fig. 3.10. The experimental results and simulation curves for reduction of CTC with Zn powder.

Fig. 3.11. The experimental results and simulation curves for reduction of CTC with Zn powder.

3.3.3 Kinetics of transformation

The kinetics of CTC and CF reductions were analyzed with various kinetic models. It was found that the process could be best described with the pseudo-first-order kinetic model. Therefore, the rate of reduction of chlorinated methanes can be described by the following equation (Matheson and Tratnyek, 1994; Johnson et al., 1996; Wüst et al., 1999):

$$\frac{dC}{dt} = -k_{\text{obs}}C = -k_{\text{SA}}\rho_a C \quad (3.4)$$

where C is the concentration of parent compound (mg l^{-1}), k_{obs} is the pseudo-first-order rate constant (h^{-1}), k_{SA} is the specific reaction rate constant ($\text{l h}^{-1} \text{m}^{-2}$), and ρ_a is the surface area concentration of metal in solution ($\text{m}^2 \text{l}^{-1}$).

The values of the derived reaction rate constants and corresponding half-lives for CTC and CF reductions with various zero-valent particles are shown in Table 3.2. The reaction rate constants were associated with the pH of aqueous system prevalent in the batch experiments, i.e., between 7 and 8.

It is apparent that the reaction rate constants of CTC were significantly higher than those of CF with various kinds of metal particles. This phenomenon was consistent with the thermodynamic preference, in which highly chlorinated organics were more readily reduced than lightly chlorinated ones by zero-valent metals (Matheson and Tratnyek, 1994; Johnson et al., 1996; Schrick et al. 2002; Janda et al., 2004).

Table 3.2 Values of rate constants and DCM yields for reduction of CTC and CF with various metal particles

Metal Particles	Parameters	CTC	CF
Nano-scale Ni/Fe	$k_{\text{obs}} (\text{h}^{-1})$	9.03	4.61E-1
	$k_{\text{SA}} (\text{l h}^{-1}\text{m}^{-2})$	9.22E-2	4.71E-3
	$t_{1/2} (\text{h})$	7.70E-2	1.50
	R^2	0.971	0.997
	DCM yield (%)	11%	20%
Nano-scale Fe	$k_{\text{obs}} (\text{h}^{-1})$	3.96	3.39E-2
	$k_{\text{SA}} (\text{l h}^{-1}\text{m}^{-2})$	5.99E-2	5.13E-4
	$t_{1/2} (\text{h})$	1.75E-1	20.44
	R^2	0.998	0.963
	DCM yield (%)	27%	47%
Nano-scale Fe (Lien, 2000)	$k_{\text{SA}} (\text{l h}^{-1}\text{m}^{-2})^{\text{a}}$	5.31E-4	8.41E-5
Fe powder (Baker)	$k_{\text{obs}} (\text{h}^{-1})$	1.15	5.22E-2
	$k_{\text{SA}} (\text{l h}^{-1}\text{m}^{-2})$	6.97E-3	3.15E-4
	$t_{1/2} (\text{h})$	6.02E-1	13.28
	DCM yield (%)	22%	14%
	R^2	0.958	0.995
Zn powder (Osaka)	$k_{\text{obs}} (\text{h}^{-1})$	2.29	3.98E-1
	$k_{\text{SA}} (\text{l h}^{-1}\text{m}^{-2})$	4.57E-2	7.94E-3
	$t_{1/2} (\text{h})$	3.03E-1	1.74
	R^2	0.997	0.978
	DCM yield (%)	84%	85%

The type of metal particles had profound influence on the reaction rates of CTC and CF. Specific reaction rate constant of CTC with the nano-scale Ni/Fe particles was more than 1.5 times higher than that with the nano-scale Fe particles. The difference in their reaction rates was even larger for the case of CF reduction, i.e., 8 times. The main functions of Ni (which has lower hydrogen overpotential than Fe) in the bimetallic particles were (Wang & Zhang, 1997): (i) accelerating the corrosion of Fe to increase hydrogen evolution; (ii) serving as a catalyst to accelerate the catalytic dechlorination of CTC and CF by the hydrogen produced; (iii) preventing the formation of oxide film which would block the reactive sites on Fe surface.

Comparing the nano-scale Fe with the commercial Fe, the former demonstrated over 8 times higher in specific rate constant of CTC reduction, which might be attributed to the higher surface reactivity of the lab-synthesized nano-scale particles. While the specific rate constant of CTC reduction with the nano-scale Ni/Fe was double of that with the commercial Zn, the nano-scale Ni/Fe particles demonstrated slower reaction rate in CF reduction compared to the commercial Zn. Since Zn had stronger reducing power and higher hydrogen overpotential than Fe, it had advantage in the dechlorination reaction through the direct electron transfer process (Matheson and Tratnyek, 1994; Cheng and Wu, 2000).

3.3.4. Reduction pathway

To analyze the CTC reduction pathway, the following scheme (Fig 3.12) was postulated, which was originally suggested by Lien (2000). The scheme includes both parallel and sequential pathways. While formation of other hydrocarbons (besides methane) could be significant in the prolonged experiment (at least for the case of nano-scale Fe and commercial Fe), the individual amounts of these hydrocarbons are all small or near to their detection limits, and therefore are assumed negligible. Therefore, individually, the other hydrocarbons can not be included in Fig. 3.12 and the following modeling. Nevertheless, because of the

many hydrocarbons (albeit small individual amount), their exclusion in the modeling might have some impact on the methane yield.

Fig. 3.12. Hypothetical reduction pathways for halogenated methanes and the annotated rate constants.

Due to the recalcitrance of DCM to the ZVI reduction and the absence of the chloromethane during the reduction of CTC and CF, k_{13} , k_{22} , k_{31} , k_{32} and k_{41} are treated as negligible. With this assumption and based on the pseudo-first-order kinetic model, the rate equations of CTC reduction can be simplified and expressed as follows:

$$\frac{dC_{CTC}^I}{dt} = -(k_{11}^I + k_{12}^I + k_{14}^I)C_{CTC} = -k_{obs}^{CTC}C_{CTC} \quad (3.5a)$$

$$\frac{dC_{CF}^I}{dt} = -(k_{21}^I + k_{23}^I)C_{CF} + k_{11}^I C_{CTC} \quad (3.5b)$$

$$\frac{dC_{DCM}^I}{dt} = k_{12}^I C_{CT} + k_{21}^I C_{CF} \quad (3.5c)$$

$$\frac{dC_{CH_4}^I}{dt} = k_{14}^I C_{CT} + k_{23}^I C_{CF} \quad (3.5d)$$

In the CF reduction experiments, the rate equations can be expressed as:

$$\frac{dC_{CF}^{II}}{dt} = -(k_{21}^{II} + k_{23}^{II})C_{CF} = -k_{obs}^{CF}C_{CF} \quad (3.6a)$$

$$\frac{dC_{DCM}^{II}}{dt} = k_{21}^{II}C_{CF} \quad (3.6b)$$

$$\frac{dC_{CH_4}^{II}}{dt} = k_{23}^{II}C_{CF} \quad (3.6c)$$

where k_n^I and k_n^{II} are rate constants corresponding to CTC and CF as parent substrates, respectively; C_{CTC}^I , C_{CF}^I , C_{DCM}^I and $C_{CH_4}^I$ are concentrations of the parent compound and its products for CTC reduction; and C_{CF}^{II} , C_{DCM}^{II} and $C_{CH_4}^{II}$ are concentrations of the parent compound and its products for CF reduction.

Table 3.3 Simulated rate constants (h^{-1}) of CTC and CF reduction processes with various metal particles

Metal Particles	CTC					CF	
	k_{11}^I	k_{12}^I	k_{14}^I	k_{21}^I	k_{23}^I	k_{21}^{II}	k_{23}^{II}
Nano-scale Ni/Fe	9.03	0.00	0.00	0.12	0.82	0.10	0.36
Nano-scale Fe	3.65	0.00	0.31	0.01	0.02	0.01	0.02
Fe powder	1.02	0.00	0.13	0.02	0.04	0.01	0.04
Zn powder	2.29	0.00	0.00	0.42	0.04	0.37	0.03

The prediction error sum of squares (PRESS) was used as a criterion to select the best set of rate constants. Appendix A shows the simulated rate constants and concentrations of chlorinated methanes at specific reaction times. The results which give the least value of PRESS are adopted. The best-fitted values of k_{11}^I , k_{12}^I , k_{14}^I , k_{21}^I and k_{23}^I are found as 9.03, 0.00, 0.00, 0.12 and 0.82 h^{-1} , respectively (Table 3.3). This result illustrated that all CTC was reduced through the hydrogenolysis pathway to CF (k_{11}) by the nano-scale Ni/Fe particles. The CF formed was subsequently reduced through parallel pathways including the complete reduction

pathway to methane (k_{23} , the dominant one) and hydrogenolysis pathway to DCM (k_{21}).

To further verify the validity of the transformation scheme shown in Fig. 3.12, and to show that the results of analysis of PRESS are not coincidental merely on the basis of goodness of fit criterion, a further examination of the experimental data was performed. In this analysis, the amounts of concomitantly released chloride during the initial stage of the reaction (when the parent compounds were the predominant substrates in the aqueous system) are plotted as shown in Fig. 3.13. At the initial stage of the reaction, the chloride ions in the aqueous phase were mainly liberated from the reduction of parent compound. It can be found that amount of chloride ion liberated to the aqueous phase was higher than the amount of chlorinated methanes (as parent compounds) disappeared, which indicated that the existence of parallel reduction pathway, including hydrogenolysis and elimination pathway.

Fig. 3.13. The amount of chloride ion released at the initial stage for the reduction of various chlorinated methanes with metal particles.

In the CF reduction experiment, the simulated rate constants k_{21}^{II} and k_{23}^{II} are 0.1 and 0.36 h^{-1} , respectively. With the derived reaction rate constants, the

simulated degradation and formation curves as well as the calculated chlorine mass are plotted in Figs. 3.4 and 3.5.

The simulated curves of CTC and CF reductions with the nano-scale Fe are shown in Figs. 3.6 and 3.7, respectively. The best-fitted values of k_{11}^I , k_{12}^I , k_{14}^I , k_{21}^I and k_{23}^I are 3.65, 0.00, 0.31, 0.01 and 0.02 h^{-1} , respectively. The fitted values of k_{21}^{II} and k_{23}^{II} for CF reduction are 0.01 and 0.02 h^{-1} . However, the methane yield was deviated from the simulated value after 10-h reaction, as a result of the formation the various trace amounts of hydrocarbon byproducts. The reduction of CTC was mainly through hydrogenolysis pathway to CF, followed by the parallel pathway including the complete reduction pathway to methane (k_{23}) and a hydrogenolysis pathway to DCM (k_{21}). The k_{23} -to- k_{21} ratio was lower than that with the nano-scale Ni/Fe. Thus, the inclusion of a lower hydrogen-over potential metal, such as Ni, could promote CF reduction by Fe through promoting the complete reduction pathway to methane.

The curves in Figs. 3.8 and 3.9 show the simulation results of CTC and CF reduction with the commercial Fe powder. The best-fitted values of k_{11}^I , k_{12}^I , k_{14}^I , k_{21}^I and k_{23}^I for CTC reduction are 1.02, 0.00, 0.13, 0.02 and 0.04 h^{-1} , respectively. The fitted results of k_{21}^{II} and k_{23}^{II} for CF reduction are 0.01 and 0.04 h^{-1} . The methane concentration predicted from Eqs. 3.5 and 3.6 was higher than that measured in the experiment, which was due to the exclusion of other hydrocarbon byproducts in the hypothesized reduction pathway and formulation of reaction kinetics. CTC was mainly reduced through the hydrogenolysis pathway to CF, and then the CF produced was reduced through the complete reduction pathway to methane and the hydrogenolysis pathway to DCM.

The simulated curves of CTC and CF reduction with Zn are shown in Figs. 3.10 and 3.11, respectively. The best-fitted values of k_{11}^I , k_{12}^I , k_{14}^I , k_{21}^I and k_{23}^I for CTC reduction are 2.29, 0.00, 0.00, 0.42 and 0.04 h^{-1} , respectively. The fitted values of k_{21}^{II} and k_{23}^{II} for CF reduction were 0.37 and 0.03 h^{-1} , respectively. The values indicated that CTC could only be reduced through the hydrogenolysis pathway to

CF. The production of DCM was solely due to CF reduction through hydrogenolysis pathway (k_{21}). Only a small fraction of CF was reduced directly to methane as could be inferred from the low k_{23} value. Therefore, although Zn had a stronger reducing power (with higher k_{11} and k_{21} values) compared to Fe in terms of CTC and CF reductions, its low k_{23} value compared to k_{21} resulted in the accumulation of DCM in the aqueous system. The high accumulation of DCM in the aqueous phase indicated the main shortcoming of the Zn system as compared to the Fe system.

3.3.5 Mechanism of CTC and CF reduction with nano-scale particles leading to methane production

It was proposed that the reduction of CTC was initiated by dissociative electron transfer resulting in formation of a carbon-centered radical as suggested by following reaction (Balko and Tratnyek, 1998):

The trichloromethyl radical (or dichloromethyl radical) produced could undergo several reactions. The major one is that it undergoes further electron transfer to produce CF (or DCM), as suggested by the following reaction:

Alternatively, the radicals could also react through dimerization reaction to produce various long-chain chlorinated intermediate byproducts such as hexachlorinated ethane (C_2Cl_6) and PCE (as occasionally detected in this study). Another possible reaction as suggested by Balko and Tratnyek (1998) was that the trichloromethyl radical could undergo another electron transfer process to form dichlorocarbene:

For the case of CF reduction, the higher percentage of complete reduction of CF to methane suggested that the reduction of CF might be through another mechanism. Usually in the CF reduction reaction, CF lost a proton and then a chloride ion in a sequential process to form dichlorocarbene (Smith and March, 2001):

The dichlorocarbene produced from the reactions (shown in Eqs. 3.9 and 3.10) was then hydrolyzed to give off formic acid or CO and HCl (Smith and March, 2001). The CO produced could then be reduced to methane (as well as other long chain aliphatic). Thus, the pathway illustrated by Eq. 3.10 would not produce chlorinated daughter products from CTC and CF reductions. The high yield of methane observed in this study suggested that CO was rapidly reduced to methane. The possible reduction pathways of CTC (and CF) are as depicted in Fig. 3.14.

Fig. 3.14. Reduction pathways of CTC with nano-scale particles

Fig. 3.15. Hydrogen percentages in the headspace of the batch reactor.

It is interesting to note that although hydrogen was evolved into the gas phase, which consumed hydrogen ion in the aqueous phase, the pH only increased from 7.0 to consistently around 8 at the end of the experiments. Since the complete dehalogenation of CTC and CF with the nano-scale Fe and commercial Fe powder could be accomplished after 96 h, 96 h was chosen as the sample time for measurement of hydrogen evolved (Fig. 3.15). The amount of commercial Fe powder in the batch reactor was 50 times higher than that of the nano-scale particles, while their hydrogen percentages in the head space were comparable. It suggested that the corrosion rates of the nano-scale particles were higher than that of the commercial Fe. On the other hand, hydrogenolysis pathway and the complete reduction pathway of chlorinated methanes, one consuming hydrogen ion while the other producing it, might result in self-buffering of the solution pH. Thus, pH of the solution did not increase significantly throughout the batch reaction experiments.

3.4 Conclusions

The nano-scale Ni/Fe and Fe particles were synthesized to rapidly degrade CTC and CF. Batch experiments were carried out to investigate the reduction performance of these lab-synthesized particles, as compared to commercial micro-scale Fe and Zn. Reduction pathways of CTC and CF with the synthesized nano-scale particles were also identified in this study.

The lattice structures of the nano-scale Fe and Ni/Fe particles were proved to be bcc. The TEM images showed that the particle sizes of Ni/Fe and Fe were lower than 50 nm and 100 nm, respectively. The nano-scale Ni/Fe and Fe particles demonstrated several folds of enhancement in CTC reduction rate over those achieved with the commercial micro-scale Fe powder. CTC and CF reductions with the nano-scale particles followed the pseudo-first-order kinetics with respect to the decay of parent compounds. The reduction rates of chlorinated methanes with the nano-scale particles followed the order: CTC > CF >> DCM.

The results of this chapter also indicated that zero-valent metals were not simply electron donors. They could also influence the reduction pathway of chlorinated methanes. Thus, reduction of chlorinated methanes with different metals would produce different fractionations of various byproducts. Zn was a stronger reducing agent compared to Fe, but the amount of intermediate DCM produced from the system with Zn particles as the reductant was over two times higher than that with Fe particles. In this context, Fe appeared to be a favorable reductant over Zn for its tendency to transform CTC and CF into non-chlorinated end products such as hydrocarbons. The nano-scale bimetallic Ni/Fe particles were more effective compared to the nano-scale Fe particles, in which catalytic Ni could improve the performance of Fe by producing even less DCM while enhancing the reduction rates of CTC and CF.

CHAPTER 4.

Transformation of Brominated Methanes by Nano-scale Fe and Ni/Fe

4.1 Introduction

Brominated organic compounds (BOCs) are an important group of HOCs. BOCs have natural and anthropogenic sources. BOCs can be naturally produced by algae and microorganism for communication and defense. Meanwhile, they are produced for use in organic syntheses, as ingredients in fire-resistant chemicals, as pesticides for citrus, and as antiknock additive in leaded gasoline and aviation fuel (Rajagopal et al., 1999; deWit, 2002; Loraine et al., 2002). In the presence of bromide, some BOCs are also formed as disinfection byproducts during chlorination or ozonation of water and wastewater (Hozalski et al., 2001). The major brominated disinfection byproducts of waters have been proved to include aliphatics and organics acids, such as bromoform and bromoacetic acid. Meanwhile, bromine is a catalyst for stratospheric ozone destruction. The ozone depletion could have notable consequences for biosphere and the climate. Brominated methanes, such as dibromomethane (DBM) and methyl bromide (BM), can deliver bromide to the atmosphere. The atmospheric lifetimes of DBM and BM are 0.29 year and 0.8

year, respectively (Shorter et al., 1995; Zhang et al., 1997). The longer-lived compounds can reach extremely high altitude. DBM and BM have been detected near the tropopause and the lower stratosphere (Schauffler et al., 1993). Most of the highly brominated BOCs are not readily hydrolyzed in water, with the estimated hydrolysis half-lives in the order of hundred to thousand years (Dragun, 1998), and are recalcitrant for biodegradation in the natural environment (Wever et al., 2000). Thus, it is not surprising that the toxic BOCs have been widely found in the groundwater and surface water. Therefore, an innovative technology to transform BOCs to benign end products is urgently sought.

However, the conventional biological wastewater treatment plant is not effective to transform BOCs. Thus, special destructive methods should be applied to the waters contaminated with those compounds. Typically, many methods can be applied to debrominate the BOCs, i.e. thermal decomposition, microbial debromination and abiotic debromination. Although anaerobic microbial degradation is a possible approach to accomplish debromination of some brominated flame retardants (Gerecke et al., in press), the reduction rates have been found as extremely low, with the half life at the range of dozens of days to weeks. Abiotic reductive transformation methods are more appealing, since higher reduction rates may be achieved. Zero-valent Fe can serve as a powerful reductant for abiotic reduction of BOCs (Hozalski et al., 2001; Loraine et al., 2002; Zhang et al., 2004). Bromine is more preferentially removed than chloride. (Hozalski et al., 2001; Alonso et al., 2002; Loraine et al., 2002). Loraine et al. (2002) observed the mass-transfer effects on the kinetics of 1,2-dibromoethane reduction with ZVI in the lab scale and pilot scale packed-bed reactor. Ethylene and bromide were identified as the predominant debromination products. They also concluded that mass transfer dominated in the early stage of the reaction, but once the equilibrium condition was achieved the reduction rate would be controlled by the surface reaction. Others performed batch reduction with bromoacetic acid, and acetic acid was found as the end product, which was produced through sequential hydrogenolysis (Hozalski et al., 2001; Zhang et al., 2004). Although the kinetics of debromination of tribromoacetic acid could be described with the first-order kinetics model, acceleration of the reduction

rate as the reaction proceeded was also observed (Hozalski et al., 2001). The acceleration was believed to be related to the competition for the reactive sites on the Fe surface (Hozalski et al., 2001). Zhang et al. (2004) suggested that the species with bromine substitutions and those only with chlorine substitutions might react at different sites on Fe surface. The independence of the reduction rate of tribromoacetic acid on the initial parent compound concentration indicated the mass transfer limitation in the batch reactors (Zhang et al., 2004).

To date, most of the previous studies were dedicated to shed some light on the reduction of the chlorinated organic compounds by abiotic reduction transformation with ZVI or catalytic hydrodechlorination. Unfortunately, the published reports related to the abiotic reductive transformation of BOCs with ZVI are limited. Therefore, in order to fill our knowledge gap of the dehalogenation reactions for HOCs with nano-scale ZVI, brominated methanes, including carbon tetrabromide (CTB), bromoform (BF) and dibromomethane (DBM), were chosen as the target compounds in this study. Nano-scale Fe and Ni/Fe particles were synthesized with sodium borohydride (NaBH_4) reduction method, as depicted in Chapter 3. Their reactivity and selectivity in degrading the brominated methanes were investigated and were compared with those demonstrated by the commercial Fe powder. Reduction pathways of the brominated methanes with the Fe and Ni/Fe were proposed along with their corresponding reaction rate constants.

4.2 Materials and Methods

4.2.1 Chemicals and metal particles preparation

All aqueous solutions were prepared with ultra-pure water (18.2 M Ω cm). The following chemicals were used as received without further purification: carbon tetrabromide (CTB) (Lancaster, UK), bromoform (BF) (Merck, Germany), dibromomethane (DBM) (Lancaster, UK), sodium thiosulfate pentahydrate (Ajax, Australia), sodium acetate trihydrate (Ajax, Australia), chloramine-T trihydrate (Sigma-Aldrich, USA), phenol red, sodium salt (Aldrich, USA), acetic acid (Lab-

scan, Ireland), acetone (Fisher scientific, NJ), sodium bromide (Ajax, Australia), sulfuric acid (Lab-scan, Ireland), ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (Reachim, Russia), nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) (BDH, UK), hexane (Fisher scientific, UK), methanol (J. T. Baker, NJ), calcium chloride (Ajax, Australia), Fe powder (J. T. Baker, NJ) and sodium borohydride (Lancaster, UK).

Bromomethane (BM) was prepared with sodium bromide, methanol and sulfuric acid (Morrison and Boyd, 2005). The gas produced was analyzed by gas chromatography with mass selective detector (GC/MS) to be BM. The processes of preparation and characterization of the metal particles are depicted in Chapter 3.

4.2.2 Experimental system

Batch reduction experiments were performed with 40 ml TFE-sealed screw cap bottles covered with aluminum foil. The initial pH of ultra-pure water was adjusted to 7 if necessary with 3.8 M sodium hydroxide. Basically, water was another predominant electron acceptor in the reduction system, as discussed in Chapter 2. With the corrosion of Fe in water, hydrogen gas was evolved, which would result in the hydrogen ion consumption in the aqueous phase. However, the preliminary study has shown that pH fluctuation (from 7 to around 8) was mild throughout the reaction. The minor fluctuation of pH was unlikely to affect the kinetics of debromination reaction. Therefore, no buffer or acid was added to maintain the pH value of the reduction system in all the batch experiments.

The batch system was without headspace. The metal loading for the experiments with the nano-scale particles and the commercial Fe were 2.5 g l^{-1} and 125 g l^{-1} , respectively. The relatively higher metal loading for the commercial Fe was to achieve a comparable metal surface area loading with that of the nano-scale particles ($\text{m}^2 \text{ l}^{-1}$). CTB, BF and DBM were individually introduced to the single species batch system via methanolic spikes resulting in initial concentrations of 61 μM , 82 μM and 122 μM , respectively. The bottles were placed horizontally on orbital shaker (300 rpm) at room temperature ($22 \pm 1^\circ\text{C}$) to achieve well mixed

conditions. At different reaction times, 10 ml of aqueous sample was withdrawn with gas-tight syringe from each sacrificed bottle. The sample was filtered through 0.45 μm nylon syringe filter. 1 ml of the filtered aqueous sample was extracted with 10 ml hexane for analysis of the parent and brominated byproducts with GC. 8 ml of the filtered sample was used for analysis of the dissolved bromide concentration with Flow Injection Analysis with Ion Chromatography (FIA/IC, Lachat, QuickChem 8000). The remaining 1 ml sample was analyzed for formate concentration with High Performance Liquid Chromatography (Perkins Elmer Series 200) with Polypore H column. For the GC analysis, 1 μl of the extraction was analyzed by a GC (HP 5890) with a HP-5-mega column (30 m-long $\times$ 0.53 mm-ID with 1.5 μm film thickness) and electron capture detector. The temperature conditions of the GC were as follows: initial oven temperature at 40 $^{\circ}\text{C}$ for 3 min and then raised to 180 $^{\circ}\text{C}$ for 1 min at the rate of 30 $^{\circ}\text{C}$ per min; the injector port temperature at 200 $^{\circ}\text{C}$; and the detector temperature at 250 $^{\circ}\text{C}$. After withdrawals of the aqueous sample, 10 ml headspace was left in each bottle. To quantify the evolved methane, 200 μl of headspace was withdrawn with gas tight syringe and analyzed with GC/FID directly, as depicted in Chapter 3.

To identify the other gas-phase halogenated intermediate byproducts and long-chain aliphatics produced during the reaction, batch reduction experiments were repeated with 60 ml serum bottle, so that 20 ml head space was left in each bottle. At each specific time interval, 60 μl headspace was injected into GC/MS (Agilent 6890 Series GC, 5973 Network Mass Selective Detector) with DB-5 column (30 m-long $\times$ 0.53 mm-ID with 1.5 μm film thickness). Oven temperature, injection temperature and detection temperature were set at 80 $^{\circ}\text{C}$, 280 $^{\circ}\text{C}$ and 280 $^{\circ}\text{C}$, respectively.

4.3 Results and Discussion

4.3.1 Transformation of brominated methanes

(a) Nano-scale Ni/Fe particles

Fig. 4.1 presents the experimental results and simulation curves of CTB reduction with the nano-scale Ni/Fe particles (the simulation curves are discussed in the later part). The secondary y-axis in Fig. 4.1 represents the total bromine amount (sum of the bromide ion liberated and bromine in the brominated methanes) remained in the 40 ml screw cap bottle at various reaction times. BF and DBM were the two main reactive intermediates, and they took longer reaction time to diminish once formed. Following the disappearances of BF and DBM, BM continued to accumulate in the aqueous phase and its concentration after 2 h of reaction was equivalent to 20 % of the CTB lost. Continuous measurements of the BM concentrations over 8 h indicated insignificant variation (Fig. 4.2). Methane was the main non-brominated end product of the CTB reduction. Besides methane, trace amounts of the other hydrocarbons, such as ethene and ethane etc., were occasionally detected with GC/MS (but near to their detection limits). Formate or formic acid was not found in the aqueous phase during the reaction. The amount of other hydrocarbons formed was around trace level and would not have significant influence on the total carbon mass balance in the system (Fig. 4.2). Other brominated byproducts, such as tribromoethylene and tetrabromoethylene, etc., were not detected in the aqueous phase. With the reduction of CTB, bromide ion was released into the aqueous phase. The constant amount of total bromine found throughout the experiment indicated insignificant leakage of the container, negligible sorption of brominated methanes to the particles surface, and negligible formation of other BOCs.

Fig. 4.1. Experimental results and simulation curves of CTB reduction with 2.5 g l^{-1} of the nano-scale Ni/Fe particles.

Fig. 4.2. Predominant debromination product distribution of CTB reaction with Ni/Fe particles at different reaction time.

The experimental results of BF with the nano-scale Ni/Fe particles are shown in Fig. 4.3. Compared with CTB, BF had a slightly lower reduction rate. Methane was the main non-brominated end product of the BF reduction. Total bromine masses determined at various reaction times were around 99% of the initial bromine amount ($9.35 \text{ } \mu\text{mol}$). While examination of carbon mass at 12 h of reaction revealed that methane and BM made up 79% and 18% of the total BF loss. The reasonably good mass balance achieved indicated negligible mass loss from the system and formation of other BOCs and hydrocarbons.

Fig. 4.3. Experimental results and simulation curves of BF reduction with 2.5 g l^{-1} of the nano-scale Ni/Fe particles.

Fig. 4.4. Experimental results and simulation curves of DBM reduction with 2.5 g l^{-1} of the nano-scale Ni/Fe particles.

Figure 4.4 shows the reduction results of DBM with the nano-scale Ni/Fe particles. The complete reduction of DBM could only be achieved after 3 h. The oxidation state of DBM was lower than those of CTB and BF. Thus, it showed the slowest reduction rate among the three parent compounds with the nano-scale Ni/Fe particles. BM formed accounted for around 20% of the DBM lost. Due to the low reactivity of BM with Fe, the BM would accumulate in the system. The remaining

DBM were primarily transformed to methane along with trace amounts of other hydrocarbons, such as ethane, ethene and butane, etc.

(b) Nano-scale Fe

Figure 4.5 depicts the experimental results of CTB, BF and DBM reduction with 2.5 g l^{-1} of the nano-scale Fe. In general, the reductions of brominated methanes with the nano-scale Fe showed similar trends as those with the nano-scale Ni/Fe particles. However, compared to the reduction with the nano-scale Ni/Fe particles, the reduction rates of the parent compounds and their brominated byproducts are apparently lower with the nano-scale Fe. BM was the only brominated byproduct accumulated in these systems. BM concentration was found to increase steadily and reach a plateau corresponding to 20% of the initial CTB added in the nano-scale Fe system after 14 h of reaction. Methane was the main non-brominated product detected, which accounted for 80% of CTB loss (Fig. 4.5a). Longer reaction time was needed to accomplish the dehalogenation of the less brominated methanes. The yields of recalcitrant BM produced from the debromination of different parent compounds would hover around 20% of the initial amount of parent compounds added.

Fig.4.5. Experimental results and simulation curves of brominated methanes reduction with 2.5 g l^{-1} of the nano-scale Fe particles: (a) CTB, (b) BF, and (c) DBM.

(c) Commercial Fe powder

Fig. 4.6. Experimental results and simulation curves of brominated methanes reduction with 125 g l^{-1} of the commercial Fe powder: (a) CTB, (b) BF, and (c) DBM.

Figure 4.6 shows the experimental results of brominated methanes with the commercial Fe powder. The reductions of CTB, BF and DBM were achieved over around 3 h, 4 h, and 18 h, respectively. The brominated species with higher degree

of bromination showed shorter reduction time. As indicated in the previous chapter, because the dehalogenation with ZVI was a heterogeneous reaction, availability of surface reactive sites of the reductant would influence the reduction rates of the parent compounds. Higher amount of commercial Fe powder was applied to attain comparable surface area concentration. Methane and BM were the primary end products in the system. The reduction of water with Fe would emit hydrogen gas, which would lead to pressure enhancement at the end of the experiment. The pH values in the aqueous phase hovered at around 8.

(d) Release rate of bromide ion

Fig. 4.7 The amount of bromide ion released at the initial stage for the reduction of various brominated methanes with nano-scale Ni/Fe and Fe particles.

In order to correlate the amount of bromide ion liberated with the amount of parent compound reacted, their quantities were compared at the initial stage of each batch reaction experiment. The reaction period considered in this analysis was the first sampling time for all experiments (i.e., 5 min or 10 min), except for the experiment of DBM reduction with nano-scale Fe which was 1 h. Within this initial stage of reaction, it was reasonably assumed that the bromide ions were primarily liberated from the parent compound added, much less from the reactive intermediates formed. Figure 4.7 compares the amounts of CTB, BF and DBM disappeared and the corresponding amounts of concomitantly released bromide ion

from the six experiments as indicated. The ratios of amount of parent compound disappeared to the amount of bromide released for all the six experiments were consistently below 1:1, indicating that on average more than one bromide ions were liberated from each disappeared CTB, CF or DBM molecule. This finding attested to possible occurrence of concerted debromination reaction, i.e., two or more bromine atoms might have been liberated from each of the CTB, CF and DBM molecule in their initial transformation pathway. This phenomenon is further evaluated through kinetic examination presented in the later part.

(d) Hydrogen evolution

Fig. 4.8. Hydrogen percentages in the batch reactor with headspace at 96 h.

The amount of hydrogen evolved to gas phase was also measured at 96 h and compared to the results obtained in the CTC and CF systems (Fig. 4.8). As indicated in Chapter 3, 96 h was chosen as the sample time for measurement of the evolved hydrogen. The hydrogen percentages in the gas phase of reactor with the commercial Fe powder and the nano-scale Fe were higher than 30%, which indicated water reduction by ZVI. Although the amount of Fe powder added was 50 times higher than those of the nano-scale particles, the hydrogen evolved was almost similar in these systems. The hydrogen amounts in the commercial Fe and nano-scale Fe systems were not apparently influenced by the presence of diverse species of parent compounds. Slightly less hydrogen evolutions were observed in reactions of brominated methanes with Ni/Fe particles. It was proposed that the Ni

might be a more reactive catalyst for catalytic debromination reactions, compared to the dechlorination reactions. Thus, more hydrogen was consumed acting as electron donor in Ni/Fe debromination system. C-Br bond was weaker than C-Cl bond. Apparently, the consumption of the hydrogen in the Ni/Fe system also illustrated the higher percentages of brominated methane were reduced through catalytic hydrodehalogenation process.

4.3.2 Kinetics of transformation

In order to establish the dehalogenation rate constants of various brominated methanes, transformations of brominated methanes with ZVI particles were analyzed with a pseudo-first-order kinetic model as adopted in Chapter 3:

$$\frac{dC}{dt} = -k_{\text{obs}}C = -k_{\text{SA}}\rho_a C \quad (4.1)$$

where C is concentration of the parent compound (mg l^{-1}), k_{obs} is the pseudo-first-order rate constant (h^{-1}), k_{SA} is the specific reaction rate constant ($\text{l h}^{-1} \text{m}^{-2}$), and ρ_a is the metal surface area concentration in solution ($\text{m}^2 \text{l}^{-1}$).

The derived reduction rate constants for various brominated methanes with ZVI particles are shown in Table 4.1. The R^2 obtained was higher than 0.95, which indicated the validity of the first-order kinetic model. The specific reaction rate constants of brominated methanes generally followed the sequence: $k(\text{CTB}) > k(\text{BF}) > k(\text{DBM})$. Apparently, the brominated methanes did not violate the thermodynamic preference suggesting that the highly halogenated compounds are more readily reduced than the lightly halogenated ones (Vogel et al., 1987; Matheson and Tratnyek, 1994; Johnson et al., 1996; Scherer et al., 1998; Zhang et al., 1998; Lien and Zhang, 2001), unlike the unsaturated halogenated compounds (Burris et al., 1995; Arnold and Roberts, 2000; Farrell et al., 2000). The reduction of halogenated compounds with Fe particles might involve two possible mechanisms: (1) direct electron transfer and (2) catalytic hydrodehalogenation with

evolved hydrogen (Matheson and Tratnyek, 1994). For the direct electron transfer process, the kinetics usually follows the thermodynamic preference of higher reduction rate for the highly halogenated aliphatic compounds. However, the catalytic hydrodehalogenation is likely to show an opposite trend, since the reaction occurs via the electrophilic mechanism on the adsorbed substrate where the presence of another halogen substitution may hinder its reduction reaction (Alonso et al., 2002; Keane et al., 2004). Since these two mechanisms follow the opposite trend, the dominant one would control the overall kinetics and the order of reactivities of CTB, BF and DBM. From the results of this study, it thus appeared that the brominated methanes were mainly reduced through direct electron transfer mechanism, which has been postulated to occur via the formation of outer-sphere complex with the oxide coated Fe (Totten et al. 2001).

Table 4.1 The BET surface areas of ZVIs and reduction rate constants of various brominated methanes.

Metal particles	BET surface area (m ² /g)	Kinetics			
		parameters	CTB	BF	DBM
Nano-scale Ni/Fe (4:1)	39.17	k _{obs} (h ⁻¹)	19.28	4.83	1.09
		k _{SA} (l h ⁻¹ m ⁻²)	1.97E-1	4.93E-2	1.11E-2
		t _{1/2} (h)	0.04	0.14	0.64
		R ²	0.999	0.990	0.976
Nano-scale Fe	26.45	k _{obs} (h ⁻¹)	6.65	1.21	0.18
		k _{SA} (l h ⁻¹ m ⁻²)	1.01E-1	1.83E-2	2.69E-3
		t _{1/2} (h)	0.10	0.57	3.89
		R ²	0.993	0.964	0.979
Commercial Fe (Baker)	1.32	k _{obs} (h ⁻¹)	1.51	0.71	0.20
		k _{SA} (l h ⁻¹ m ⁻²)	9.15E-3	4.28E-3	1.23E-3
		t _{1/2} (h)	0.46	0.98	3.41
		R ²	0.984	0.996	0.953

The specific reduction rate constants of brominated methanes with the nano-scale Fe were apparently higher than those with the commercial Fe. The most possible reason for this is that the smaller particle size provides higher density of reactive sites. The observed reduction rate constants of CTB, BF and DBM with the nano-scale Ni/Fe were around 2.9, 4.0 and 6.1 times higher than those of the nano-scale Fe, respectively. This was attributable to the presence of Ni. Besides, as a lower hydrogen over-potential metal than Fe, Ni could form galvanic cell with Fe and thus accelerated Fe dissolution and reduced accumulation of the oxide films that could passivate the Fe surface reactive sites (Schrack et al., 2002; Wu and Ritchie, 2006).

4.3.2 Derivation of kinetic rate constants for various reaction processes

The hypothetical transformation scheme for reduction of brominated methanes, which involves both parallel and sequential pathways, is shown in Chapter 3 (Fig. 3. 12). The possible formations of larger BOCs and hydrocarbons are not reflected, because of their insignificance as observed in this study. Based on the scheme (Fig. 3.12) and the pseudo-first-order kinetic model, the following rate equations are constructed.

For CTB reduction:

$$\frac{dC_{CTB}^I}{dt} = -(k_{11}^I + k_{12}^I + k_{13}^I + k_{14}^I) C_{CTB}^I = -k_{obs}^I C_{CTB}^I \quad (4.2a)$$

$$\frac{dC_{BF}^I}{dt} = -(k_{21}^I + k_{22}^I + k_{23}^I) C_{BF}^I + k_{11}^I C_{CTB}^I \quad (4.2b)$$

$$\frac{dC_{DBM}^I}{dt} = -(k_{31}^I + k_{32}^I) C_{DBM}^I + k_{12}^I C_{CTB}^I + k_{21}^I C_{BF}^I \quad (4.2c)$$

$$\frac{dC_{BM}^I}{dt} = -k_{41}^I C_{BM}^I + k_{13}^I C_{CTB}^I + k_{22}^I C_{BF}^I + k_{31}^I C_{DBM}^I \quad (4.2d)$$

$$\frac{dC_{CH_4}^I}{dt} = k_{14}^I C_{CTB}^I + k_{23}^I C_{BF}^I + k_{32}^I C_{DBM}^I + k_{41}^I C_{BM}^I \quad (4.2e)$$

For BF reduction:

$$\frac{dC_{BF}^{II}}{dt} = -(k_{21}^{II} + k_{22}^{II} + k_{23}^{II})C_{BF}^{II} = -k_{obs}^{II}C_{BF}^{II} \quad (4.3a)$$

$$\frac{dC_{DBM}^{II}}{dt} = -(k_{31}^{II} + k_{32}^{II})C_{DBM}^{II} + k_{21}^{II}C_{BF}^{II} \quad (4.3b)$$

$$\frac{dC_{BM}^{II}}{dt} = -k_{41}^{II}C_{BM}^{II} + k_{22}^{II}C_{BF}^{II} + k_{31}^{II}C_{DBM}^{II} \quad (4.3c)$$

$$\frac{dC_{CH_4}^{II}}{dt} = k_{23}^{II}C_{BF}^{II} + k_{32}^{II}C_{DBM}^{II} + k_{41}^{II}C_{BM}^{II} \quad (4.3d)$$

For DBM reduction:

$$\frac{dC_{DBM}^{III}}{dt} = -(k_{31}^{III} + k_{32}^{III})C_{DBM}^{III} = -k_{obs}^{III}C_{DBM}^{III} \quad (4.4a)$$

$$\frac{dC_{BM}^{III}}{dt} = k_{31}^{III}C_{DBM}^{III} - k_{41}^{III}C_{BM}^{III} \quad (4.4b)$$

$$\frac{dC_{CH_4}^{III}}{dt} = k_{32}^{III}C_{DBM}^{III} + k_{41}^{III}C_{BM}^{III} \quad (4.4c)$$

where k_n^I , k_n^{II} and k_n^{III} are reduction rate constants (h^{-1}) when CTB, BF and DBM were used as the parent compounds, respectively; C_{CTB}^I , C_{BF}^I , C_{DBM}^I , C_{BM}^I and $C_{CH_4}^I$ are concentrations ($mg\ l^{-1}$) of the parent compound, intermediates and end products for CTB reduction; C_{BF}^{II} , C_{DBM}^{II} , C_{BM}^{II} and $C_{CH_4}^{II}$ are concentrations ($mg\ l^{-1}$) of the parent compound, intermediates and end products for BF reduction; C_{DBM}^{III} , C_{BM}^{III} and $C_{CH_4}^{III}$ are concentrations ($mg\ l^{-1}$) of the parent compound, intermediates and end products for DBM reduction.

Table 4.2 Derived reduction rate constants of brominated methanes with ZVIs

Parent Compounds	ZVI	k ₁₁	k ₁₂	k ₁₃	k ₁₄	k ₂₁	k ₂₂	k ₂₃	k ₃₁	k ₃₂	k ₄₁
CTB	Fe (Baker)	1.02	0.00	0.01	0.48	0.91	0.00	0.28	0.05	0.21	0.00
	Nano Fe	6.65	0.00	0.00	0.00	1.84	0.03	0.03	0.04	0.16	0.00
	Nano Ni/Fe	12.80	3.46	0.49	2.53	10.84	0.20	2.80	0.63	1.72	0.00
BF	Fe (Baker)	-	-	-	-	0.59	0.02	0.10	0.10	0.33	0.00
	Nano Fe	-	-	-	-	1.21	0.00	0.00	0.09	0.34	0.00
	Nano Ni/Fe	-	-	-	-	2.63	0.15	2.05	0.54	1.52	0.00
DBM	Fe (Baker)	-	-	-	-	-	-	-	0.05	0.16	0.03
	Nano Fe	-	-	-	-	-	-	-	0.04	0.14	0.00
	Nano Ni/Fe	-	-	-	-	-	-	-	0.33	0.76	0.10

Note: (i) The unit of the rate constants is h⁻¹.

(ii) k₁₁ to k₁₄ are the rate constants for CTB reduction, k₂₁ to k₂₃ are the rate constants for BF reduction, and k₃₁ and k₃₂ are the rate constants for DBM reduction.

The curves in Figs. 4.1 to 4.6 represent the simulation results. The prediction error sum of square (PRESS) was used as the criterion to assess the fitness of the chosen values for the rate constants. The set of k_n values which gave the lowest PRESS were adopted as the best fitted values and they are listed in Table 4.2. Because the formation of the larger BOCs and hydrocarbons is excluded in the preceding modeling, there are slight deviations in the predicted results for the concentrations of the compounds analyzed, especially methane.

4.3.3 Reduction pathways and mechanisms with nano-scale particles

From the results presented in Table 4.2, a scheme summarizing the overall reduction pathways for brominated methanes with the nano-scale Fe and Ni/Fe

particles is proposed (Fig. 4.9). Two reductive dehalogenation pathways are indicated: hydrogenolysis (replacement of halogen by hydrogen) and elimination (elimination of two halogen atoms). The main reduction pathway for CTB involved coupling of sequential hydrogenolysis and elimination mechanisms, indicated as: $\text{CTB} \rightarrow \text{BF} \rightarrow \text{DBM} \rightarrow \text{CH}_4$.

Fig. 4.10. Reduction pathways for the reduction of brominated methanes with the nano-scale Fe and Ni/Fe particles.

For the hydrogenolysis pathway of brominated methanes, the initial step has been reported to follow a dissociative electron transfer process resulting in the formation of radicals, including $\cdot\text{CBr}_3$, $\cdot\text{CHBr}_2$, etc. (Balko and Tratnyet, 1998; Totten et al., 2001, O'Loughlin et al., 2003). The competition between the two possible subsequent reactions, i.e., second electron transfer process to form a carbene ($\cdot\text{CBr}_3 + e^- \rightarrow \text{:CBr}_2 + \text{Br}^-$) and combination with the hydrogen atom to form a hydrogenolysis product ($\cdot\text{CBr}_3 + \text{H} \rightarrow \text{CHBr}_3$), would result in the different brominated intermediate product distributions. The combination of the radicals ($\cdot\text{CBr}_3$ and $\cdot\text{CHBr}_2$) with the dissociated hydrogen atom appeared to be the dominant process during CTB and BF reductions. For the complete reduction

pathway ($\text{CTB} \rightarrow \text{CH}_4$) and the two bromine elimination pathway ($\text{CTB} \rightarrow \text{DBM}$), the dibromocarbene ($:\text{CBr}_2$) might be the possible intermediate which was produced through α -elimination of CTB. The $:\text{CBr}_2$ formed could be transformed via parallel pathways too, i.e., combination with two atomic hydrogens to form DBM ($:\text{CBr}_2 + 2\text{H} \rightarrow \text{CH}_2\text{Br}_2$) and hydrolysis to CO followed by reduction to methane (and other aliphatics) in the presence of Fe or Ni. The possibility of the formation of aliphatics from CO reduction with Fe has been proved by previous researchers (Hardy and Gillham, 1996; Deng et al., 1997; Lien, 2000).

As indicated in the Chapter 3, while the reductions of CF with nano-scale particles were mainly through the complete reduction pathway to methane, the reductions of BF were however mainly through hydrogenolysis pathway to DBM. The differences of the predominant reduction pathways of CF and BF reduction were related to the properties of the halogen substitute. Usually, $(:\text{CCl}_3)^-$ was proposed to be a possible reactive intermediate during the complete reduction CF (Smith and March, 2001). The first step of forming this intermediate was to release a proton. The electron acceptance ability of bromide was lower than that of chloride. Therefore, the stability of $(:\text{CBr}_3)^-$ will be less thermodynamically favorable. Thus, the complete reduction pathway of BF to methane with the nano-scale particles was not the favorable pathway.

An interesting observation was that a rather high fraction of DBM was reduced through the complete reduction pathway to methane, which was not the case for CTB and BF. The complete reduction pathway of DBM was also proved in Fig. 4.10. Apparently, the reduction of each mole of DBM released 1.82 moles of bromide ions, which attested to the predominance of concerted reductive debromination mechanism for direct DBM reduction to methane. The reduction of DBM might be through formation a metallic carbonoid species (BrCH_2FeBr). The process might be similar to the Simmons-Smith reaction (Morrison and Boyd, 2005), and is represented as follow:

BrCH_2FeBr was an organoiron compound which could then combine with adsorbed atomic hydrogen to produce methane, as represented below:

Only trace amounts of larger BOCs and their reductive debrominated hydrocarbons such as ethene, ethane, etc., were detected in the experiment because of limited collision of the radicals ($\cdot\text{CBr}_3$ and $\cdot\text{CHBr}_2$) formed. The radicals were short-lived because once formed, most of them were destroyed by combination with atomic hydrogen or electron on metal surface. Therefore, they were less possible to escape from the metal surface and collide with one other to form larger molecules.

Fig. 4.10. The amount of bromide ion released for the reduction of DBM with nano-scale Ni/Fe and Fe particles.

Due to its low reactivity with Fe and Ni/Fe, BM produced could not undergo further hydrodehalogenation, as shown by its low k_{41} values. It was the main halogenated byproduct accumulated in the ZVI system. As presented in Figs 4.1 and 4.3 to 4.6, at the end of the batch experiments, BM produced could reach a concentration level equivalent to 16% to 24% of the initial parent compound concentration. However, the incomplete reduction of brominated methanes by the

ZVI systems to methane is unlikely to pose environmental concerns. The BM remained in water may not pose concern, because it is readily hydrolyzed in water into innocuous products, such as methanol, with its hydrolysis half-life of 20 days (Mabey and Mill, 1978). It is worth to note that the lightly brominated methane is more susceptible to hydrolysis compared to the polybrominated methane (Mabey and Mill, 1978), which counters the thermodynamic rule for their abiotic reductive dehalogenation. Moreover, a less halogenated compound tends to be more biodegradable than its polyhalogenated counterpart. Thus, although the ZVI technology may fail to reduce BM byproduct to methane within a timescale practical to its application, it can be complemented with hydrolysis and biodegradation processes occurring in natural environmental systems to achieve complete dehalogenation within a reasonable timescale.

4.4 Conclusions

Kinetic and mechanistic examinations of the abiotic reductive dehalogenation of the various brominated methanes with the Ni/Fe and Fe particles were performed. The reduction processes followed pseudo-first-order kinetics. The reduction rates followed the order: CTB > BF > DBM >> BM. Addition of Ni to the Fe/water system and using nano-scale particles were the two effective methods to improve the performance of the ZVI system for abiotic reduction of the brominated methanes. A scheme of reduction pathway for the brominated methanes with the nano-scale Fe and Ni/Fe particles is proposed in this chapter. The major degradation pathway for CTB, BF and DBM led to their complete reductions to methane, while the minor pathway led to formation of BM. The reductions of CTB and BF were mainly through hydrogenolysis reaction. The catalytic effects of Ni not only increased the specific reduction rate of the target compounds by the ZVI, but also changed the significance of each parallel reduction pathway and therefore influenced the brominated product distribution. With this mechanistic insight into the complex dehalogenation mechanisms of the brominated methanes with the nano-scale Fe particles system, one can design the best-suited ZVI treatment

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system, avoiding the unfavorable pathways that may lead to formation of undesirable intermediates.

CHAPTER 5.

Transformation of Halogenated Methanes with Nano-scale Pd/Fe

5.1. Introduction

Catalytic hydrodehalogenation with hydrogen donor is one of the important subsets of abiotic reductive transformation of HOCs with ZVI. Typically, many noble metals, such as Pd, Pt, Au, Cu, and Ag etc., can serve as the catalysts (Heinrichs et al., 1997; Schüth and Reinhard, 1998; Bonarowska et al., 2001a; Lin et al., 2004). Among all the catalyst, Pd has been proved to be the most effective species for dehalogenation reaction (Urbano and Marinas, 2001; Lin et al., 2004). Hydrogen gas was the most favorable hydrogen donor for the dehalogenation of HOCs in the previous studies (Deshmukh and d'Itri, 1998; Lowry and Reinhard, 2000; Simagina et al., 2003; Nutt et al, 2005). Other water-soluble reductants, such as formic acid, hydrazine and isopropanol, etc., are also possible alternative to hydrogen (Kopinke et al, 2004).

Introduction of low hydrogen over-potential metals, such as Pd, to ZVI system may increase the effects of catalytic dehalogenation of the ZVI system, which will apparently enhance the reactivities of ZVI particles (Wang and Zhang, 1997; Elliott and Zhang, 2001; Lien and Zhang, 2001; Lin et al., 2004). The interaction between the two metals can also influence the reactivity of the particles. Coating the catalyst on the ZVI surface or forming bimetallic alloy are two possible approaches to prepare the bimetallic particles (Zhang et al., 1998; Schrick et al., 2002).

Improvements of Pd/Fe over the Fe system include two aspects, i.e. enhancement of the degradation rate of the target compounds and reduction in accumulation of the harmful by-products (Schreier and Reinhard, 1995; Wang and Zhang, 1997; Liu et al., 2001; Kim and Carraway, 2003; Xu et al., 2005a). Lin et al. (2004) reported that with Pd/Fe particles, the observed reduction rate constant of TCE was higher compared to other bimetallic particles, such as Pt/Fe, Ru/Fe and Au/Fe, and moreover no accumulations of chlorinated products were observed during the TCE reduction.

The reduction mechanisms with the presence of Pd are still inconclusive. Cheng et al. (1997) hypothesized that the adsorbed hydrogen gas by Pd would form a reducing species ($\text{Pd}\cdot\text{H}_2$), in which the hydrogen gas intercalated into the elemental Pd lattice. Another possible explanation is that the Pd activated hydrogen atom ($\text{Pd}\cdot\text{H}^*$) can attack the carbon-halogen bond to achieve dehalogenation, while Fe transfers the electron from the metal surface to carbon-halogen bond (Zhang et al., 1998; Kopinke et al., 2004).

Linear free energy relationships (LFERs) have been successfully used in many chemical reactions. The development of transition state theory provides the theoretical bases for the LFERs. The resulting LFERs can be applied to predict the reactivity of the relevant compounds which are not found in the original data set (Scherer et al., 1998). Meanwhile, they are also important tool for mechanistic analyses (Johnson et al., 1996; Liu et al., 2000; Totten and Roberts, 2001). Based

on the kinetic constants reported by Johnson et al. (1996), Scherer et al. (1998) developed the LFERs for dechlorination of chlorinated aliphatics with ZVI. Burrow et al. (2000) also established a satisfactory correlation relationship between the dechlorination rate constants and the vertical attachment energies (VAEs). Lien (2000) observed that the correlation relationships were usually weak for the nano-scale Pd/Fe system. Although the kinetic data are limited to establish reliable quantitative LFERs, one conclusion can be achieved, that is the higher degrees of halogenation showing higher reduction rates (Johnson et al., 1996; Scherer et al., 1998). Liu et al. (2000) observed a linear relationship between the logarithms of reduction rate constants and the carbon-chloride dissociation bond enthalpies for the chlorinated alkanes. Compared to chlorinated alkanes, the reduction rates of chlorinated alkenes are less sensitive to the degree of chlorination, which suggest that most of the electron transfer in the alkenes might occur in the lowest energy π level (Scherer et al., 1998; Liu et al., 2000).

In this study, the 0.2% Pd/Fe (w/w) and 1% Pd/Fe (w/w) particles were synthesized as the bimetallic reductants. Chlorinated and brominated methanes with different degrees of halogenation were the target compounds for treatment. The objectives of this study included: (i) presenting the characterization of the nano-scale Pd/Fe particles; (ii) identifying the degradation kinetics, pathways and reduction mechanisms for the halogenated methanes with the nano-scale Pd/Fe particles and the influence of Pd content; (iii) analyzing correlation between the observed reduction rate constants and the associated thermodynamic constants; (iv) developing the two-parameter regression relationships for kinetic prediction.

5.2 Materials and Methods

5.2.1 Chemicals

Chemicals used are as follows: carbon tetrabromide (CTB) (Lancaster, UK), bromoform (BF) (Merck, Germany), dibromomethane (DBM) (Lancaster, UK), carbon tetrachloride (CTC) (BDH, UK), chloroform (CF) (Merck, Germany),

methylene chloride (DCM) (J. T. Baker, NJ), palladium acetate ($\text{Pd}(\text{C}_2\text{H}_3\text{O}_2)_2$) (Merck, Germany), sodium thiosulfate pentahydrate (Ajax, Australia), sodium acetate trihydrate (Ajax, Australia), chloramine-T trihydrate (Sigma-Aldrich, USA), phenol red, sodium salt (Aldrich, USA), acetic acid (Lab-scan, Ireland), acetone (Fisher scientific, NJ), sodium bromide (Ajax, Australia), sulfuric acid (Lab-scan, Ireland), ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (Reachim, Russia), ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) (Sigma Aldrich, USA), mercuric thiocyanate ($\text{Hg}(\text{SCN})_2$) (Merck, Germany), hexane (Fisher scientific, UK), methanol (J. T. Baker, NJ), calcium chloride (Ajax, Australia), sodium chloride (Lancaster, UK), and sodium borohydride (Lancaster, UK), methane (5%, National Oxygen Pte Ltd, Singapore). All chemicals were used as received without further purification. Bromomethane (BM) was prepared with sodium bromide, methanol and sulfuric acid (Morrison and Boyd, 2005). The gas produced was analyzed by gas chromatography with mass spectrometry (GC/MS) to be BM. All aqueous solutions were prepared with ultra-pure water (18.2 M Ω cm).

5.2.2 Preparation and characterization of Pd/Fe particles

The nano-scale Fe particles were synthesized by adding sodium borohydride (NaBH_4) solution to ferrous sulfate solution. The precipitates were washed with ultra-pure water (>300 ml) and separated using vacuum filter through 1.2- μm glass fiber membrane. The wet particles were separated into three parts. One part of the nano-scale Fe particles was directly stored in the freeze-drier for further usage. The other two parts were separately coated with Pd by re-suspending the Fe particles in the acetone solution of palladium acetate. The Pd loadings were 0.2% and 1% of the amount of Fe added (w/w), respectively. After adding the particles to the acetone solution, the color of the solution turned from orange to almost achromaticity within a few minutes, indicating that the aqueous Pd^{2+} has been reduced to particulate Pd^0 . At last, the particles were filtered through the 1.2 μm glass fiber membrane and dried in the freeze-drier over night before use.

Brunauer-Emmett-Teller (BET) surface area analysis of the lab synthesized nano-scale Fe and Pd/Fe particles were carried out with Quanta Chrome autosorb automated gas absorption system. The particles were out-gassed with nitrogen at 300 °C over 3 h. X-ray diffraction (XRD) analysis of mineralogical characteristics of the Pd/Fe particles were carried out with Bruker D8 advanced XRD diffractometer. Transmission electron microscope (TEM) images were obtained with JOEL electron microscope (JEM-2010). Small amount of metal particles were put into pure ethanol and dispersed in ultrasonic bath before mounted on the grid. The surface elemental composition of Pd/Fe particles was analyzed with scanning electron microscope (SEM, JSM-6360) combined with energy-dispersive X-ray spectrometry (EDX, JED-2003 X-ray analyzer).

5.2.3 Experimental system

Batch reduction experiments were performed with 40 ml TFE-sealed screw cap bottles covered with aluminum foil. The batch system was carried out without headspace. The metal loading in the experiments with the nano-scale particles was 2.5 g l⁻¹. CTB, BF, DBM, BM, CTC, CF and DCM were individually introduced to the single-species batch system via methanolic spikes resulting in initial concentrations of 61, 82, 122, 125, 122, 167 and 110 µM, respectively. The bottles were placed on an orbital shaker horizontally which operated at 300 rpm at room temperature (22±1 °C). The initial pH of the solutions was adjusted to 7 with sodium hydroxide solution. No buffer solution was added to control the pH of the solution. Other conditions for the experimental systems were the same as those described in Chapter 3. The analysis methods of halogenated methanes, methane and dissolved halogen ions have been depicted in Chapters 3 and 4 in detail.

5.3 Results and Discussion

5.3.1 Characteristics of Pd/Fe particles

Fig. 5.1. SEM-EDX elemental map of Pd/Fe particles: (a) SEM image of 0.2% Pd/Fe (b) elemental map of Fe for 0.2% Pd/Fe (c) elemental map of Pd for 0.2% Pd/Fe (d) SEM image of 1% Pd/Fe (e) elemental map of Fe for 1% Pd/Fe (f) elemental map of Pd for 1% Pd/Fe

Based on the SEM-EDX elemental map of the Pd/Fe particles, Pd was observed to distribute evenly on the Fe surface in the region of the SEM images (Fig. 5.1). Because the Pd was mainly coated on the Fe surface, the surface content of Pd was apparently higher than the theoretical Pd content. For instance, for the 1% Pd/Fe, over 8% surface mass was covered by Pd. For the 0.2% Pd/Fe, Pd was

around 0.32% of the total surface mass. Nutt et al. (2005) also observed similar results of nano-scale Pd/Au particles. The existence of O in the SEM-EDX spectrum (figure not shown) indicated that a small fraction of surface Fe might have been oxidized to Fe_2O_3 or Fe_3O_4 and thus a small fraction of the zero-valent Fe might be covered by a thin discontinuous oxide film.

Fig. 5.2. TEM images of Pd/Fe particles: (a) fresh 0.2% Pd/Fe, (b) fresh 1% Pd/Fe.

Diameters of the synthesized Fe, 0.2% Pd/Fe and 1.0% Pd/Fe particles observed through TEM were smaller than 100 nm (Fig. 5.2). Because of the magnetic effects between the small particles, the particles aggregated together to form microscale or larger chain structures. The two different synthesized particles appeared to have a similar morphology, and the BET surface areas of the Pd/Fe particles were rather similar to that of the synthesized Fe particles (presented in Chapter 3), which was around $26 \text{ m}^2 \text{ g}^{-1}$. The structures of their crystals were observed with XRD. Peaks identified on the XRD patterns were confirmed to be associated with the body centered cubic Fe (Fig. 5.3). Due to the small percentages of Pd in the Pd/Fe particles, peaks belonging to Pd were not noticeable on the XRD patterns.

Fig. 5.3. XRD patterns for 0.2% nano-scale Pd/Fe particles.

5.3.2 Transformation of halogenated methanes

(a) Transformation of chlorinated methanes with 0.2% Pd/Fe

Figure 5.4a presents the experimental results for the reduction of CTC with the 0.2% Pd/Fe. CTC is one of the most reactive target compounds in this study. Its concentration was reduced to below GC detection limit ($0.15\ \mu\text{M}$) within 40 min. CF was initially the main intermediate byproduct, which later disappeared after 6 h. With the reduction of CTC and CF, DCM concentration increased steadily to over 11% of the initial CTC concentration. Methane was the main non-chlorinated end product which was detected in the gas phase. Other chlorinated dimerization products, such as PCE and TCE, were only occasionally detected in the aqueous phase with concentrations of around their GC detection limits. During the experiment, the total chlorine mass (comprising those in the chlorinated methanes and the liberated chloride) remained in the batch solution system at different reaction times were higher than 95% of its initial mass ($19.6\ \mu\text{mol}$). It indicated the insignificant leakage of the container, negligible sorption of HOCs to the metal surface, and negligible formation of other HOCs during the CTC reduction.

Experimental results of CF reduction with the 0.2% Pd/Fe is shown in Fig. 5.4b. Compared with CTC, CF reacted relatively slowly (as compared to CTC) with

the Pd/Fe particles to yield DCM and methane, both were the major products. DCM accounted for 25 % of the CF lost. To confirm the persistency of DCM in the presence of the Pd/Fe bimetallic particles, a separate experiment was performed in which DCM was reacted with the 0.2% Pd/Fe over 25 h. However, it was found that DCM loss was lower than 5 % over this period. Thus, the production of methane and other trace amounts of non-chlorinated hydrocarbons from the CTC or CF appeared to be through the reductive elimination pathway instead of the sequential hydrogenolysis pathway (e.g. CTC $\rightarrow$ CF $\rightarrow$ DCM $\rightarrow$ CM $\rightarrow$ Methane).

Fig. 5.4. Experimental results and simulation curves for reduction of chlorinated methanes with 2.5 g l^{-1} of the 0.2 % Pd/Fe particles: (a) CTC, and (b) CF.

The reductions of CTC and CF with the 1% Pd/Fe particles were also examined. The complete reductions of CTC and CF were achieved within 10 min and 5 h, respectively (figures not shown). DCM was still stable in the presence of the 1% Pd/Fe particles, and it accounted for 12% and 20% of the initial masses of CTC and CF in the respective experimental systems.

(b) Transformation of brominated methanes with 0.2% Pd/Fe

Figure 5.5 shows the experimental results and simulation curves of CTB, BF and DBM reductions with the 0.2 % Pd/Fe. Apparently, the brominated methanes were reduced more rapidly compared to the chlorinated methanes. Complete reductions of CTB, BF and DBM were achieved within 20 min, 40 min and 3 h, respectively. Methane was the main end products found in the three experiments. BF and DBM, as the two reductive intermediate byproducts for CTB reduction, disappeared from the system shortly after their appearances (Fig. 5.5a). BM concentration continued to increase to 10% of the initial CTB concentration after 1 h, and further monitoring up to 8 h did not show significant change of its concentration. Trace amounts of dimerization products were also detected in the aqueous phase by GC/MS. The total bromine hovered around 95% of its initial mass throughout the experiment.

The reduction of BM with the 0.2% Pd/Fe and 1% Pd/Fe particles was further examined by performing separate batch experiments in which BM was the parent species. The experiment showed that around 75% of BM was transformed into methane by the 1% Pd/Fe over 46 h. However, with the 0.2% Pd/Fe, its transformation was negligible over the same period.

Fig. 5.5. Experimental results and simulation curves for reduction of brominated methanes with 2.5 g l^{-1} of the 0.2 % Pd/Fe particles: (a) CTB, (b) BF, and (c) DBM.

5.3.3 Kinetics of transformation and the influence of Pd content

The transformations of halogenated methanes were analyzed with pseudo-first-order kinetic model which has been shown appropriate by the previous researchers (Matheson and Tratnyek, 1994; Johnson et al., 1996; Arnold and Roberts, 1998; Wüst et al., 1999) and with the Ni/Fe particles in this study:

$$\frac{dC}{dt} = -k_{\text{obs}}C = -k_{\text{SA}}\rho_a C \quad (5.1)$$

where C is the concentration of parent compound in the aqueous phase (mg l^{-1}), k_{obs} is the observed reduction rate constant of the parent compound (h^{-1}), k_{SA} is the specific reduction rate constant ($\text{l h}^{-1} \text{m}^{-2}$), and ρ_a is the surface area concentration of the metal particles ($\text{m}^2 \text{l}^{-1}$).

Table 5.1 Values of reduction rate constants of halogenated methanes with nano-scale Pd/Fe and Fe particles

		CTC	CF	CTB	BF	BDM	BM
0.2% Pd/Fe	$k_{\text{obs}} (\text{h}^{-1})$	10.64	0.47	17.41	6.48	1.96	0.00
	$k_{\text{SA}} (\text{l h}^{-1} \text{m}^{-2})$	1.61E-1	7.11E-3	2.63E-1	9.80E-2	2.96E-2	0.00
	$t_{1/2} (\text{h})$	0.07	1.47	0.04	0.11	0.35	-
1% Pd/Fe	$k_{\text{obs}} (\text{h}^{-1})$	56.04	0.89	>40	>40	8.35	3.96E-2
	$k_{\text{SA}} (\text{l h}^{-1} \text{m}^{-2})$	8.47E-1	1.35E-2	>6.05E-1	>6.05E-1	1.26E-1	5.99E-4
	$t_{1/2} (\text{h})$	0.01	0.78	<0.02	<0.02	0.08	17.50
Fe ^a	$k_{\text{obs}} (\text{h}^{-1})$	3.96	3.39E-2	6.65	1.21	0.18	0.00
	$k_{\text{SA}} (\text{l h}^{-1} \text{m}^{-2})$	5.99E-2	5.13E-4	1.01E-1	1.83E-2	2.72E-3	0.00
	$t_{1/2} (\text{h})$	0.18	20.45	0.10	0.57	3.85	-

Note: a. results are shown in previous chapters.

The observed reduction rate constants of halogenated methanes with the various Pd/Fe particles are presented in Table 5.1. In this study, without adding buffer solution, the pH value would only increase marginally from 7 to around 8. Thus, the minor fluctuation of pH would not influence much on the reduction rates, as pointed out by Matheson and Tratnyek (1994). The smallest R^2 achieved in the regression with the first-order kinetics model are higher than 0.964, as shown in Fig. 5.6, which presents the results of degradation of various parent compounds with the Fe, 0.2% Pd/Fe and 1% Pd/Fe particles. Also included in Table 5.1 are the results obtained with the nano-scale Fe particles for comparison. In general, the specific reduction rate constants of brominated methanes were higher than those of their chlorinated counterparts. The most possible reason is that the C-Br bond is weaker than the corresponding C-Cl bond. Another consistent finding was that the highly halogenated methanes showed relatively higher reduction rate than the lightly halogenated ones. This phenomenon is consistent with the thermodynamic preference suggesting that highly oxidized species are more susceptible to reduction.

The observed dehalogenation rate constants of the halogenated methanes with the Pd/Fe particles were also higher than those with the nano-scale Fe, as depicted in Fig. 5.6. For CTB and BF degradation with the 1% Pd/Fe particles, a very high reduction rate constants was also observed (results not shown in Figs. 5.6c and 5.6d), whose rate constants are given in Table 5.1. The sharp increases in the reduction rates of halogenated methanes with Pd/Fe were attributed to the noble metal Pd. Pd, as relatively lower hydrogen over-potential metal in the Fe/water system, could form galvanic cell with Fe. In the presence of cathodic Pd, the corrosion rate of anodic Fe increased, resulting in higher hydrogen evolution and fresher surface condition of the Fe particles. Besides, in the presence of atomic hydrogen (H) produced from water reduction with Fe, Pd could also act as catalyst in the catalytic hydrodehalogenation reaction.

Fig. 5.6. Plot of $\ln(C_0/C)$ as a function of reduction time: (a) CTC, (b) CF, (c) CTB, (d) BF, and (e) DBM.

It is worth noting that in this study, although the increase in Pd content could shorten the half life of the reduction reaction for the halogenated methanes, the intermediate byproduct distribution was not significantly affected. On the other

hand, excessive Pd might not be beneficial to the dehalogenation reaction. As indicated in the EDX elemental map and spectrum, the surface Pd content increased sharply with the percentage of Pd loaded to Fe particles content. However, Pd, as a noble metal catalyst, could not serve as an electron donor directly. Thus, if the Fe surface was completely covered by Pd, the reduction rate of parent compounds would decrease sharply due to the blocking of internal Fe from water in the system. This has been confirmed by Lien (2000) who found that the reduction rate of TCE could reverse if Pd content became too high (>5%). Another observation was that the influences of Pd content on the kinetics varied for different parent compounds. For instance, the observed reduction rate constant of CTC with the 0.2% Pd/Fe was more than two times of that with the nano-scale Fe. While the reduction rates for CF and DBM with the 0.2% Pd/Fe were over 10 times of those with the nano-scale Fe. Further increase in Pd content would reverse the trend. With the 1% Pd/Fe particles, the enhancement of CTC reduction rate over that with the 0.2% Pd/Fe was higher than the case for CF. Thus, the optimal Pd contents in the Pd/Fe particles were different for different parent compounds.

5.3.4 Reduction pathways

The reduction of halogenated methanes could involve parallel and sequential pathways. The hypothesized reduction pathways of various halogenated methanes with the Pd/Fe and Fe particles and the annotated rate constants are shown in Chapter 3 (Fig. 3.12). Since the possible formations of other HOCs and hydrocarbons were insignificant, they are not reflected in the scheme.

For degradations of CX_4 , CHX_3 or CH_2X_2 as the parent compounds, the generalized rate equation can be expressed as follows:

$$\frac{dC_i}{dt} = - \left(\sum_{j=1}^{5-i} k_{ij} \right) C_i \quad (5.2)$$

where k values are rate constants (h^{-1}), i is the counter for the types of parent compounds (e.g., 1 for CX_4 , 2 for CHX_3 and 3 for CH_2X_2), j is the counter for the hypothesized pathways as annotated in Fig. 3.12. For instance, if CTB is the parent compound, thus Eq. 5.2 could be expressed as follows:

$$\frac{dC_{\text{CTB}}}{dt} = - \left(\sum_{j=1}^4 k_{1j} \right) C_{\text{CTB}} \quad (5.3)$$

For CHX_3 , CH_2X_2 or CH_3X produced as intermediate products, the generalized rate equation for their formations/degradations can be expressed as follows:

$$\frac{dC_m}{dt} = \sum_{i=1}^{m-1} k_{i,m-i} C_i - \left(\sum_{j=1}^{5-m} k_{mj} \right) C_m \quad (5.4)$$

where m is the counter for the type of intermediate products (e.g., 2 for CHX_3 , 3 for CH_2X_2 and 4 for CH_3X). If CTB was the parent compound, BF was one of the brominated intermediates during the CTB dehalogenation. Thus, based on Eq. 5.4, the equation can be expressed as follows:

$$\frac{dC_{\text{BF}}}{dt} = k_{11} C_{\text{CTB}} - \left(\sum_{j=1}^3 k_{2j} \right) C_{\text{BF}} \quad (5.5)$$

On the basis of the halogenated products distribution found from the experiments, each reduction rate constant, k , can be calculated. The prediction error sum of square (PRESS) was used as the criterion to assess the goodness of fit of the chosen k values to the experimental results. The set of k values which gave the lowest PRESS value was chosen.

Table 5.2 Best-fitted rate constants (h^{-1}) of halogenated methanes with nano-scale metallic particles

Parent Compound	ZVI	k_{11}	k_{12}	k_{13}	k_{14}	k_{21}	k_{22}	k_{23}	k_{31}	k_{32}	k_{41}
	Fe ^a	6.65	0.00	0.00	0.00	1.84	0.03	0.03	0.04	0.16	0.00
CTB	0.2% Pd/Fe	7.75	3.58	0.30	5.78	5.31	0.19	4.08	1.12	5.49	0.05
	Fe ^a	-	-	-	-	1.21	0.00	0.00	0.09	0.34	0.00
BF	0.2% Pd/Fe	-	-	-	-	4.22	0.64	1.62	0.27	3.29	0.03
	Fe ^a	-	-	-	-	-	-	-	0.04	0.14	0.00
DBM	0.2% Pd/Fe	-	-	-	-	-	-	-	0.54	1.42	0.03
	1% Pd/Fe	-	-	-	-	-	-	-	1.89	6.46	0.14
	Fe ^b	3.65	0.00	0.00	0.31	0.01	0.00	0.02	0.00	0.00	0.00
CTC	0.2% Pd/Fe	6.04	0.07	0.00	4.53	0.12	0.00	0.48	0.00	0.00	0.00
	1% Pd/Fe	37.98	0.00	0.00	18.06	0.34	0.00	1.54	0.00	0.00	0.00
	Fe ^b	-	-	-	-	0.01	0.00	0.02	0.00	0.00	0.00
CF	0.2% Pd/Fe	-	-	-	-	0.12	0.00	0.35	0.00	0.00	0.00
	1% Pd/Fe	-	-	-	-	0.19	0.00	0.70	0.00	0.00	0.00

Note: a. Figures are shown in chapter 4.

b. the data are from chapter 3.

The best-fitted rate constants are presented in Table 5.2. As can be inferred from the table, reduction of CTB with the 0.2 % Pd/Fe was through two pathways, including hydrogenolysis pathway to BF (k_{11}) and reductive elimination pathway to DBM (k_{12}) and methane (k_{14}). For the reduction of BF, the hydrogenolysis pathway to DBM (k_{21}) was favored over the reductive elimination pathway to methane (k_{23}). However, the reduction of DBM was through a different mechanism in which a higher fraction of DBM was reduced through reductive elimination to methane, avoiding the formation of the unfavorable intermediate (i.e., BM). The main reduction pathway of CTC was hydrogenolysis pathway to CF. With Pd added to the Fe/water system, the significance of reductive elimination pathway of CTC to

methane (k_{14}) increased. The main reduction pathway of CF was through reductive elimination pathway to methane (k_{23}).

Based on the findings from this chapter, the following reduction dehalogenation reactions are postulated. The reductions of CTC and CTB were initiated by dissociative electron transfer process resulting in the formation of carbon-centered radicals such as $\cdot\text{CCl}_3$ and $\cdot\text{CBr}_3$ (i.e., $\text{RX} + \text{e}^- \rightarrow \cdot\text{R} + \text{X}^-$). Subsequently, the radicals could undergo another electron transfer process to combine with the dissociated hydrogen and form the less halogenated molecules (i.e., $\cdot\text{R} + \text{e}^- + \text{H}^+ \rightarrow \text{RH}$). Alternatively, the radicals could undergo another dissociative electron transfer process to form carbenes, including $:\text{CCl}_2$ and $:\text{CBr}_2$. Hydrolysis of the carbenes formed would then produce the completely dehalogenated product, such as carbon monoxide, which would be further reduced to methane.

However, the continuous dissociative process might not provide a valid explanation to the higher fraction of CF reduction via the complete reduction pathway (k_{23}). As concluded in Chapter 3, the reduction of CF might be initiated by release of a proton to form carbanion ($:\text{CCl}_3^-$) and then a chloride ion to form $:\text{CCl}_2$ [i.e., $\text{CHCl}_3 \rightarrow :\text{CCl}_3^- + \text{H}^+ \rightarrow :\text{CCl}_2 + \text{Cl}^- + \text{H}^+$], rather than through hydrogenolysis to form $\cdot\text{CHCl}_2$ radical and then CH_2Cl_2 (DCM). Although BF shares an analogous molecular structure with CF, the main reduction pathway of BF was hydrogenolysis, as evidenced by its high hydrogenolysis rate constant (k_{21}). Bromine is a weaker electron acceptor than chlorine, and thus the process of releasing a proton from BF may be thermodynamically less favorable. Therefore, the dissociative electron transfer step that led to formation of $\cdot\text{CHBr}_2$ and then CH_2Br_2 (DBM) was the dominant process during the BF reduction, as evidenced by the predominance of k_{21} over k_{23} (Table 5.2).

In the reduction of DBM with the nano-scale Pd/Fe and Fe particles, a higher percentage (> 70%) of DBM was reduced through the elimination pathway to non-brominated products. The complete reduction of DBM might proceed

through formation of carbonoid complex (i.e., BrCH_2FeBr) (Morrison and Boyd, 2005). The combination of the carbonoid complex with the dissociated hydrogen led to formation of the complete dehalogenation products, such as methane, as evidenced by the high k_{32} value compared to k_{31} .

5.3.5 Establishing one-parameter linear free energy relationships for analysis of reduction mechanism

According to the transition state theory, a relationship should exist between the reaction rate constant of a reaction and the energy required by the reactants to reach a postulated transition state, as expressed by the following equation (Liu et al., 2000):

$$k_{\text{SA}} = A \exp(-\Delta G^*/RT) \quad (5.6)$$

where k_{SA} is the specific reduction rate constant ($\text{l h}^{-1} \text{ m}^{-2}$), ΔG^* (kJ mol^{-1}) is the activation energy for the transition intermediate which represents the rate limiting step of the overall reduction pathway, A is the reaction-dependent preexponential factor, R is the universal gas constant ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature (K). The ΔG^* can be related to the corrected standard free energy change for the reaction, ΔG^0 (kJ mol^{-1}), according to Marcus theory (Curtis, 1991; Totten and Robert, 2001):

$$\Delta G^* = \frac{\lambda}{4} \left(1 + \frac{\Delta G^0}{\lambda} \right)^2 \quad (5.7)$$

where λ is the reorganization energy (kJ mol^{-1}). Thus, if combining Eqs. 5.6 and 5.7 and taking the logarithm on both sides, there exists a parabolic relationship between $\log k_{\text{SA}}$ and ΔG^0 . However, the main assumption of Marcus theory is that the electron transfer processes are through the outer-sphere electron transfer reaction, which is less possible for the reductive dehalogenation reaction since the formation of radical is an irreversible process (Curtis, 1991; Totten and Robert, 2001). Despite

this discrepancy, previous researchers argued that the linear relationship between $\log k_{SA}$ and ΔG^0 could still be approximately applied (Totten and Roberts, 2001). Previous researchers also proved the possibility of the regression between $\log k_{SA}$ and one-electron reduction potential (E_1) (Roberts et al., 1996; Scherer et al., 1998; Liu et al., 2000). As E_1 can be correlated with bond dissociation energy (BDE) and lowest unoccupied molecular orbital energy (E_{LUMO}) (Totten and Roberts, 2001), all these thermodynamic parameters may be also used as the descriptors in this study. According to Eberson (1987), λ is an adjustable fitting parameter which does not vary with different halogen substitutions. On the other hand, another large contributor to ΔG^0 calculation is the Gibbs free energy of the halide ions which is produced during the dehalogenation of the parent compounds (Totten and Roberts, 2001). The solvation of the halide ion is another important driving force for the dehalogenation reaction, thus separate correlations of the reduction rates of chlorinated and brominated compounds with E_1 will give more reliable LFERs (Eberson, 1987; Totten and Roberts, 2001). Therefore, separating the HOCs into groups and establishing the regression relationship respectively are two important aspects to achieve acceptable LFERs.

The thermochemical data corresponding to the formation of carbon-centered radicals and the theoretically calculated reduction potentials and energies are shown in Table 5.3. The correlations between the specific reduction rate constants and E_1 are shown in Fig. 5.7. Due to insufficient data, the regression process could not be applied. Meanwhile, the offset of E_1 between each group of the compounds was due to the different solvation effects of bromide and chloride ions (Totten and Roberts, 2001). The BDE is the energy required to homolytically fracture a chemical bond, thus it also relates to the energy of formation of carbon centered radical. Based on this concept, BDE and E_1 express similar mechanism. Comparing to E_1 , in the reduction of halogenated methanes, the E_2 values (in Table 5.3) correspond to the overall reduction potential of hydrogenolysis reaction ($RX + H^+ + 2e^- \rightarrow RH + X^-$). On the other hand, the first electron transfer step is the rate limiting step during the hydrogenolysis and α -elimination of halogenated methanes (Balko and Tratnyek, 1998). Thus, E_1 might be a more suitable descriptor compared to E_2 for describing

the reduction of halogenated methanes. As evidenced by Fig. 5.7, E_1 values show an acceptable correlations with the $\log k_{SA}$ ($R^2 > 0.94$) in the reduction of brominated methanes with the Pd/Fe and Fe particles. In comparison, a weaker correlation between BDE and $\log k_{SA}$ ($R^2 > 0.88$) is found.

Table 5.3 Summary of thermodynamic data and descriptor parameters for correlation analysis of the halogenated methanes

Species	ΔG_f (kJ/mol) ^a	H_c^b	E_2 (V) ^c	Radical	$\Delta H_f(R\cdot)$ (kJ/mol)	$\Delta S_f(R\cdot)$ (J/mol K)	E_1 (V) ^c	E_{LUMO} (eV) ^e	BDE (kJ/mol) ^f
CTC	-53.5	3.04E-02	0.70	$\cdot CCl_3$	77.0 ^d	299.3 ^d	0.17	-3.28	294
CF	-70.1	3.67E-03	0.59	$\cdot CHCl_2$	98.2 ^d	265.9 ^d	-0.23	-2.54	322
DCM	-68.8	3.25E-03	0.52	$\cdot CH_2Cl$	118.7 ^d	238.5 ^d	-0.40	-1.74	335
CM	-58.4	8.82E-03	0.50	-	-	-	-	-	-
CTB	65.2	1.00E-05	0.71	$\cdot CBr_3$	207.1 ^e	335.6 ^e	0.05	-4.18	240
BF	7.44	5.35E-04	0.57	$\cdot CHBr_2$	188.3 ^e	303.7 ^e	-0.33	-3.45	283
DBM	-16.2	9.30E-04	0.49	$\cdot CH_2Br$	169.0 ^e	257.1 ^e	-0.52	-2.59	296
BM	-28.2	6.24E-03	0.50	$\cdot CH_3$	147.0 ^d	195.2 ^d	-0.62	-1.55	297
Methane	-50.8	6.58E-01	-	-	-	-	-	-	-

Note: ^a Lide, 2006; ^b H_c indicates Henry's Law constant ($\text{atm m}^3 \text{mol}^{-1}$) as derived from Lyman et al., 1982; and Totten and Roberts, 2001; ^c pH = 7, $\{Cl^-\} = \{Br^-\} = 0.1 \text{ mM}$; ^d Bylaska et al., 2002; ^e Totten and Roberts, 2001; ^f BDE $(R-X) = \Delta H_f^0(R\cdot) + \Delta H_f^0(X\cdot) - \Delta H_f^0(RX)$ (Liu et al., 2000).

Fig. 5.7. Correlation relationship between $\log(k_{SA})$ and E_1 for reduction with the 0.2% Pd/Fe.

In order to confirm whether the first electron transfer process of the elimination pathway is the rate limiting step during the reduction, LFERs are developed for the hydrogenolysis rate constants (indicated as k_{11} , k_{21} and k_{31}) with E_1 for the case of brominated methanes. It appears that the correlations of the hydrogenolysis rate constants with E_1 are weaker ($R^2 > 0.78$) than the correlation of the $\log k_{SA}$ with E_1 (with $R^2 > 0.94$). This observation suggests that for reduction of brominated methanes, the first electron transfer process might be the rate limiting step for both hydrogenolysis and elimination processes which concertedly affecting k_{SA} , rather than the hydrogenolysis process alone.

5.3.6 Two-parameter regression for kinetics prediction

Goss and Schwarzenbach (2001) proposed that poly-parameter regression could be a powerful tool in the field of environmental partition processes. Liu et al (2003) also developed two-parameter linear relationships for the dechlorination rate constants of chlorobenzenes, which provide the possibility of application of multi-parameter linear regression to dechlorination reactions. The E_{LUMO} and standard heat of formation were two independent descriptors in their optimal model. The lowest unoccupied molecular orbital (LUMO) is defined as the frontier molecular

orbit where the electron transfer takes place (Fleming, 1976). Totten and Roberts (2001) observed that there exists strong linear relationship between E_1 , E_2 , E_{LUMO} and BDE, which indicated that these four parameters are linearly dependant. Philosophically, for describing the reductive dehalogenation mechanism, E_1 , E_2 , BDE appears to be more suitable than E_{LUMO} . However, for kinetics prediction, LFERs with E_{LUMO} is better than E_1 , E_2 and BDE, since there is only one E_{LUMO} value for each target compound and the E_{LUMO} value is not to be influenced by the solvation of different halide ions. It essentially avoids the complication arising from influence of different reduction pathways and different group of halogenated compounds. Therefore, E_{LUMO} is chosen as one independent variable for quantitative analysis of LFERs.

Table 5.4 The specific reduction rate constants with different contents of Pd in the Pd/Fe particles.

No	Compounds	E_{LUMO} (eV)	Theoretical Pd Content	$\log k_{\text{SA}}$ (observed)
1	CTB	-4.18	0	-1.00
2	CTB	-4.18	0.2%	-0.58
3	BF	-3.45	0	-1.74
4	BF	-3.45	0.2%	-1.01
5	DBM	-2.59	0	-2.57
6	DBM	-2.59	0.2%	-1.53
7	DBM	-2.59	1%	-0.90
8	BM	-1.55	1%	-3.22
9	CTC	-3.28	0	-1.22
10	CTC	-3.28	0.2%	-0.79
11	CTC	-3.28	1%	-0.07
12	CF	-2.54	0%	-3.29
13	CF	-2.54	0.2%	-2.15
14	CF	-2.54	1%	-1.87

Meanwhile, Pd content is another important parameter which can influence the reduction kinetics significantly. The influences of Pd content on the reduction kinetics are usually related to the properties of parent compounds, as discussed in the preceding part. Therefore, Pd content is chosen as another variable, and the statistical analysis indicated that Pd content and E_{LUMO} were two independent parameters. Table 5.4 summarizes the observed reduction rate for each parent compounds with different Pd/Fe particles.

As illustrated in the preceding discussion, there is a linear relationship between E_{LUMO} and $\log k_{\text{SA}}$. However, the relationship between the Pd content and the specific reduction rate constant is still not very clear. To simplify the process of establishing correlation, second order polynomial equation is applied to establish the relationships. Basically, six terms are included in the general equation as follows:

$$\log k_{\text{SA}} = a + b \cdot E_{\text{LUMO}} + c \cdot \text{Pd}_{\text{content}} + d \cdot E_{\text{LUMO}} \text{Pd}_{\text{content}} + e \cdot E_{\text{LUMO}}^2 + f \cdot \text{Pd}_{\text{content}}^2 \quad (5.8)$$

where a, b, c, d, e, f are constants; $\text{Pd}_{\text{content}}$ is the theoretical Pd content of the Pd/Fe particles (w/w); E_{LUMO} is the lowest unoccupied molecular orbital energy (eV); and k_{SA} is the specific reduction rate constant of halogenated methanes ($\text{l h}^{-1} \text{ m}^{-2}$). The analysis of variance (ANOVA) is used to check the correlations of each term and the standard errors of the model. Figure 5.8 shows the flow chart of the regression process. Firstly, the equation is regressed with the six coefficients. Although the adjusted R^2 is around 0.82, some p-values of the coefficients are higher than 0.01, which indicated that it was uncertain to reject the hypothesis that the coefficient is not equal to 0. Therefore, the term E_{LUMO}^2 with the highest p-value (0.72) of the coefficient can be deleted from the regression. The regression process was repeated until the p-values of the coefficients were all lower than 0.01.

Fig. 5.8. Flow chart of the regression process.

For the reduction of halogenated methanes, the simulation equation is eventually derived to the following:

$$\log k_{SA} = -5.48 - 47.87 \times E_{LUMO} \cdot Pd_{content} - 1.15 \times E_{LUMO} \quad (5.9)$$

The R^2 of this equation is 0.89, and the adjusted R^2 is equal to 0.76. The correlation between the observed and the predicted $\log k_{SA}$ is shown in Fig. 5.9. The numbers in Fig. 5.9 are corresponding to the numbers of experiment listed in Table 5.4. Tables 5.5 and 5.6 show ANOVA for the two-parameter model and the standard errors of the coefficients. The F value (in Table 5.5), which is higher than 3.98 ($f_{0.05, 2, 11}$) value, indicated the existence of significant relationship between the $\log k_{SA}$ and the two descriptors E_{LUMO} and $Pd_{content}$. Figure 5.10 shows the contour plots of

the combined effects of E_{LUMO} and Pd content on the specific reduction rate constants.

Fig. 5.9. The plot of observed $\log k_{\text{SA}}$ versus their predicted values.

Table 5.5 ANOVA for the two-parameter regression model

Source of variation	Degree of freedom	Sum of Squares	Mean square	F	Significance F
Regression	2	9.73	4.86	21.83	0.00014804
Residual	11	2.455	0.22		
Total	13	12.18			

Table 5.6 Coefficients and their standard errors

	Coefficients	Standard Error	P-value
Intercept	-5.48	0.62	2.42E-6
E_{LUMO}	-47.87	12.15	2.31E-3
Pd content	-1.15	0.19	7.57E-5

Fig. 5.10. Contour plot of the combined effects of E_{LUMO} and Pd content on the specific reduction rate constants.

In principle, the derived equation can be used to predict the rate of reduction of any halogenated methanes, such as bromochloromethane (CH_2BrCl), dibromochloromethane (CHBr_2Cl) and dibromodifluoromethane (CBr_2F_2), etc., with the nano-scale Pd/Fe as the reductant. It is worth to note that the range of the Pd content should be strictly no more than 1%, since the dechlorination rates would be inhibited at the higher theoretical Pd content (e.g., >5% according to Lien, 2000). To get the precise prediction for the reduction rate with the palladized iron particles of higher Pd content (>1%), more experiments should be done with those Pd/Fe particles.

The preceding correlation analysis for reductive dehalogenation of halogenated methanes with the nano-scale particles is still in a formative stage. To perform a more rigorous study and derive robust regression relationships applicable to diverse groups of halogenated aliphatics, the pre-requisite is to gather sufficient amount of data sets of reduction rate constants for these compounds with the nano-scale particles of interest.

5.4 Conclusions

The reduction rates of brominated methanes with the lab-synthesized nano-scale Pd/Fe particles were higher than those of their chlorinated counterparts. The reduction rate followed the order: CTB > CTC > BF > DBM > CF >> BM. Addition of Pd to the nano-scale Fe particles could apparently improve the performance of the nano-scale Fe system. However, increasing the Pd content from 0.2 % to 1 % could only enhance the reduction rate of target compound, but the byproducts distribution did not change significantly. The reduction of CTC proceeded mainly through hydrogenolysis pathway to CF, which would then primarily completely dechlorinated to non-chlorinated products. However, the main reduction pathway of CTB with the Pd/Fe particles followed sequential hydrogenolysis to DBM and then α -elimination to non-brominated products. The validity of the proposed transformation pathway was further tested with thermodynamic consideration. A stronger correlation between the observed

reduction rate constants (k_{SA}) and E_1 indicated that the first electron transfer process might be the rate limiting step during the reduction of brominated methanes. Meanwhile, E_{LUMO} would be the best descriptor for kinetics prediction for other halogenated methanes. Two-parameter regression relationship has been developed for kinetics prediction in this study. However, the adjusted R^2 is only around 0.76. Therefore, more work should be done in the future on this aspect to establish robust and versatile regression relationships which allow first-cut prediction of reaction rates for reductive dehalogenation of various halogenated aliphatics. With the established regression relationships, it may essentially eliminate the need to perform the experiment on individual HOCs which can be exhaustive.

CHAPTER 6.

Influences on the Reduction Kinetics of Carbon Tetrachloride: Solution Matrix and Regeneration of the Nano-scale Particles

6.1 Introduction

As indicated in the previous chapters, treatment with nano-scale Fe and bimetallic particles have been proven to be a feasible option for removal of halogenated organic compounds (HOCs). Since the dechlorination reaction with ZVI is largely controlled by surface reactions, the reactivity of ZVI is influenced by the water chemistry of the aqueous phase and the surface characteristics of ZVI. Usually, the water chemistry of groundwater or wastewater will change from site to site. Basically, pH is a “master variable” in water chemistry and geochemistry, which influences the amount and chemical form of many organic and inorganic substances dissolved in waters. Many researchers indicated that pH value has some influence on the HOCs dechlorination rate and ZVI dissolution (Matheson and Tratnyek, 1994, Chen et al., 2001). However, significance of the pH influence is

related to the pH range (Chen et al., 2001). A general conclusion is that the reduction rate will decrease with the increase of pH value. Other factors that have been found influencing the dechlorination kinetics include: (i) the presence of non-reactive competitors, such as amphiphilic compounds which often appear in groundwater and wastewaters along with chlorinated solvent contaminants, (ii) the presence of alternative oxidants, such as nitrate, sulfate, phosphate, perchlorate, etc., and (iii) the surface characteristics of ZVI.

The most commonly found natural amphiphiles in wastewater and natural waters are natural organic matters (NOMs). The main effects of amphiphiles in the aqueous phase include four aspects, e.g. solubilization enhancement, sorption enhancement, competitive sorption and mediation of electron transfer (Tratnyek et al., 2001). Klausen et al. (2003) investigated the effects of NOMs on the granular Fe toward the chlorinated carbons and nitroaromatic compounds in their column reduction system. They indicated that the solute could adversely affect Fe reactivity. The experiment conducted by Tratnyek et al. (2001) showed that humic acids have a greater inhibitory effect than fulvic acids on CTC reduction. However, the effects were not significant over the range of conditions investigated in their study. Doong and Lai (2005) found inhibitory effects of NOM on PCE dechlorination with palladized Fe particles. Interestingly, after 24 h equilibrium between the humic acid and Pd/Fe, the PCE dechlorination rate would increase with increasing concentration of humic acid. It proved that humic acids could serve as electron-transfer mediators.

Anthropogenic surfactants are another important group of amphiphiles often found in the wastewaters and natural water systems. Anthropogenic surfactants are applied extensively to increase the mobility of the non-aqueous phase liquids for in-situ groundwater remediation and ex-situ soil washing process. Therefore, the coexistences of the various surfactants and COCs are ubiquitous in natural and engineered environmental systems. Surfactants are generally grouped as anionic, nonionic, cationic, or amphoteric (Porter, 1994). The influences of surfactant on reduction kinetics of COCs are usually related to the species of parent compound

and the surfactant. Loraine (2001) observed that although the aqueous surfactant concentration would increase the surface concentrations of PCE and TCE on iron particles, the reactivity of Fe particles was still inhibited with higher anionic surfactant concentration. Zhang et al. (2002) found that the reduction rate constant of PCE increased by a factor of 5 with the presence of the cationic surfactant hexadecyltrimethyl ammonium. However, Tratnyek et al. (2001) concluded that the influence of surfactants on the Fe reduction system was moderate, and was not likely to be significant in field application.

Compared to non-reductive effect induced by the amphiphiles, the effects of the alternative oxidants on the dechlorination kinetics with ZVI are more complex. One group of such oxidants are inorganic dissolved metal ions, such as Se, Cr, Hg, and Cu, etc. (Blowes et al., 2000). Their removal mechanisms include adsorption, precipitation, and biological transformation. Another group of oxidants can only compete with HOCs for the metal surface reactive sites, and the reduction products will not show the catalytic effect for the dechlorination reactions. For instance, nitrate, as one of the most common groundwater contaminants, can be reduced by ZVI (Cheng et al., 1997; Huang et al., 1998; Choe et al., 2000; 2004; Huang and Zhang, 2004; Liou et al., 2005). Nitrate reduction has been observed to occur via direct reduction by Fe and indirect reduction by hydrogen formed from the corrosion of Fe (Huang et al., 1998). The reduction products include nitrite, nitrogen and ammonia, depending on the reduction conditions (Huang et al., 1998; Choe et al., 2000; Yang and Lee, 2005). Since the coexistence of nitrate and HOCs are ubiquitous, the competition effects between these two oxidants have been investigated. Some researchers indicated that nitrate had detrimental effects on the reduction of HOCs with zero-valent Fe (Siantar et al., 1996). Nitrate, as an oxidizing inhibitor, can passivate the metal surface via reacting with Fe and lead a sharp increase of pH and redox potential. Thus, the oxide film formed will accumulate on the metal surface and act as a barrier for further reaction of the metal (Ritter et al., 2002).

For the surface characteristic of ZVI, two aspects should be considered. Firstly, as indicated in the previous chapters, the bimetallic particles could improve the performance of ZVIs. Secondly, with the elapse of reaction time, a layer of oxide film would accumulate on the ZVI surface, which would apparently affect the reactivity of ZVI (Wang and Zhang, 1997). It has been observed that a number of oxide species, including Fe_2O_3 , FeOOH , and Fe_3O_4 , would form as a result of the corrosion of ZVI in water (Ritter et al., 2002). The formation of passivated film, which serves as semiconductors or insulators, will hinder the direct electron transfer process. Meanwhile the catalytic hydrodehalogenation reaction will also be inhibited, since hydrogen evolution is less thermodynamically favorable on the surface covered by ferric oxide film. Several methods have been used to treat the oxide-film covered ZVIs, including acid washing, chloride treatment, and hydrogen reducing process (Matheson and Tranyek, 1994; Gotpagar et al., 1999; Korte et al., 2000; Lin and Lo, 2005). Some researchers observed that besides passivation by oxide film, the reduced sulfur species which was produced from the sulfate reduction by ZVIs, can also result in permanent poisoning of the catalyst (e.g. Pd) (Korte et al., 2000).

In this part of study, the main objectives were devoted to the following: (i) to observe the pH influence on the dechlorination kinetics of CTC with the synthesized nano-scale particles; (ii) to examine the effects of NOM, surfactants (e.g. cationic, nonionic, and ionic surfactants); and anion matrix, including nitrate, nitrite, sulfate and sulfite, on the dechlorination kinetics; and (iii) to assess the effectiveness of sodium borohydride in regenerating the aged nano-scale particles.

6.2 Materials and Methods

6.2.1 Chemicals and nano-scale particles preparation

Chemicals used are as follows: potassium nitrate (Merck, Germany), o-phosphoric acid (85%, Fisher Scientific, NJ), potassium sulfate (Merck, Germany), potassium sulfite (Merck, Germany), potassium dihydrogen phosphate (Ajax,

Australia), and di-potassium hydrogen phosphate (Ajax, Australia), sodium dodecyl sulphate (SDS) (J. T. Baker, NJ), nonylphenol ethoxylate (NPE) (Aldrich, USA), dodecyl pyridinium chloride (DPC) (TCI, Japan), n-hexadecane (Merck), humic acid (sodium salt) (Aldrich, USA). Other chemicals used are depicted in the former chapters. The processes of preparation and characterization of metal particles are depicted in chapter 3 and chapter 5. The properties of surfactants used in this chapter are listed in Table 6.1.

Table 6.1 Summary of surfactant properties

	Type	Formula	CMC (mM)
SDS	Anionic	$\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$	8
NPE	Non-ionic	$\text{C}_9\text{H}_{19}(\text{C}_6\text{H}_4)(\text{OCH}_2\text{CH}_2)_9\text{OH}$	0.1
DPC	Cationic	$\text{C}_{12}\text{H}_{25}\text{Cl}(\text{C}_5\text{H}_5\text{N})$	17.5

In the experiments for regeneration of nano-scale particles, 1 l screw cap bottle was filled with 1 l ultra-pure water, 2.5 g nano-scale particles and 20 mg CTC were added in the solution. The bottles were put on the orbital shaker (300 rpm) horizontally. After 5 day-reaction, the particles were filtered through 0.2 μm cellulose acetate membrane filter and washed with 100 ml ultra-pure water. One fraction of the used nano-scale particles was dried in the freeze drier for further usage. Another fraction of the used particles was re-suspended in 300 ml ultra-pure water. NaBH_4 solution was prepared by dissolving 3 g NaBH_4 in 200 ml ultra-pure water. The reductant solution was added drop-wise to the mixture. The solution was shaken on the orbital shaker for 20 mins, until no bubbles were released from the solution. The black particles formed were separated with vacuum filter and washed with over 100 ml of ultra-pure water for 3 times and then rinsed with 20 ml of acetone. At last, the regenerated particles were dried in the freeze drier over night. The regenerated particles were black and appeared to be similar to their virgin counter parts.

X-ray diffraction (XRD) analysis of mineralogical characteristics of the lab synthesized and regenerated nano-scale particles were carried out with Bruker D8

advanced XRD diffractometer. The surface element composition of the nano-scale particles was analyzed with scanning electron microscope (SEM, JSM-6360) combined with energy-dispersive X-ray spectrometry (EDX, JED-2003 X-ray analyzer). Transmission electron microscope (TEM) images were obtained with JOEL electron microscope (JEM-2010). The detailed procedures are described in Chapter 3.

6.2.2 Experimental system with fresh nano-scale particles

(a) pH influence

To investigate the pH influence on the system, phosphate based buffer was used to stabilize the pH of the solution at a constant value for each reduction experiment. Different ratios of 0.05 M H_3PO_4 , KH_2PO_4 and K_2HPO_4 were mixed together to obtain desired pH values which were set at 4, 6 and 8. Since the pH buffer capacity would be exhausted over long reaction time, CTC was chosen as the only target compound investigated, because the experiment could be terminated within 2 h. Other experimental conditions were as illustrated in Chapter 3. At each specific time, 5 ml aqueous phase was withdrawn from the sacrificed bottles for CTC concentration determination with GC. After 2-h reactions, iron phosphate precipitations were observed in the bottles containing solutions with pH 4 and pH 6.

(b) Effect of solution matrix

In this part of experiment, nano-scale 0.04% Pd/Fe particles were used as the reductant. Batch reduction experiments were performed with 60 ml TFE-sealed serum bottles covered with aluminum foil. The initial pH of ultrapure water was adjusted to 7.0 with 3.8 M sodium hydroxide. The batch system was carried out with 20 ml headspace left in each bottle. The metal loading in the experiments with the nano-scale particles was 0.5 g l^{-1} . CTC was introduced to the batch reduction system through a methanol spike resulting in initial concentrations of $520 \text{ }\mu\text{M}$. The bottles were placed on an orbital shaker horizontally which operated at 300 rpm at room temperature ($22 \pm 1 \text{ }^\circ\text{C}$). CTC concentrations were determined by periodically remove $80 \text{ }\mu\text{l}$ gas phase from the sacrificed vials with gas tight syringe. The

withdrawn gas was then analyzed by gas chromatograph (HP5890) with flame ionization detector.

Similar experimental protocol was used to evaluate the adsorption of amphiphile (e.g. humic acid, SDS, NPE, and DPC) on the nano-scale Fe, except that no CTC was injected to the serum bottle. The aqueous amphiphile concentrations in the single species batch system were determined by total organic carbon (TOC) (ASI-V, Shimadzu, Japan) after dilution with ultrapure water to a TOC concentration lower than 500 mg l⁻¹. The aqueous samples were filtered through 0.45 µm nylon syringe filter.

6.3 Results and Discussions

6.3.1 pH value influences

Figure 6.1 shows the reduction kinetics of CTC in non-buffered solution and phosphate buffer solution (pH 4, 6, and 8) with the three different nano-scale particles. The reduction rates of CTC in the phosphate buffer solution were lower than those in solutions without buffer, which indicated that phosphate ion would inhibit the CTC reduction. As stated in Section 6.2.2, the concentration of all the buffer solutions was 0.05 M. Thus, the inhibition effect related to the different concentrations of buffer solution should be consistent for all experiments.

Fig. 6.1. Reduction kinetics of CTC at various pH values with: (a) nano-scale Fe particles, (b) nano-scale Ni/Fe particles, and (c) nano-scale 0.2% Pd/Fe.

In the phosphate buffered system, the reduction rate of CTC decreased with the increase of pH. The reason of the high dechlorination rates in the solution with

lower pH was higher corrosion rate of the Fe particles in the solution with low pH. The high Fe corrosion rate would increase the amount of electron released, which would accelerate both the direct dechlorination and catalytic dechlorination reactions. Meanwhile, the reduction was observed to follow pseudo-first-order kinetics with respect to the parent compound. However, at pH 8, the kinetics of CTC degradation with the nano-scale Fe appeared to slightly deviate from the first-order model after 1 h of reaction (Fig. 6.1a). The deviation might be related to the accumulation of the ferric oxide and ferric phosphate precipitate on the particle surface at pH 8. In the bimetallic particle system, no apparent deviation from first-order kinetics was observed in the bimetallic system at pH 8. It was due to the galvanic effect between the metals with different hydrogen over-potential, which could help to preserve the fresh condition of Fe particles.

6.3.2 Influences of humic acid

Fig. 6.2. Experimental results of CTC reduction with Pd/Fe in the presence of humic acid at various concentrations.

Figure 6.2 shows the results of CTC reduction with the nano-scale Pd/Fe in the presence of humic acid. The kinetics of CTC reduction in ultrapure water is presented by the solid line. The CTC reduction with the Pd/Fe particles generally followed a pseudo-first order kinetics. With the increase of the humic acid concentration, the reduction rate of CTC decreased gradually. In the presence of humic acid, the reduction rates within the initial 2 min were apparently lower than

Table 6.2 Summary of reduction rate constants of CTC with Pd/Fe

	Concentration	TOC (mg l ⁻¹)	k _{obs} (min ⁻¹)	t _{1/2} (min)	R ²
Ultrapure water		0.00	0.309±0.035	2.24±0.22	
Humic Acid	50 mg l ⁻¹	12.8	0.174	3.98	0.949
	200 mg l ⁻¹	57.9	0.129	5.37	0.967
	400 mg l ⁻¹	124.7	0.116	5.98	0.982
	1000 mg l ⁻¹	318.5	0.082	8.45	0.924
DPC	1.75 mM	324.6	0.09	7.70	0.985
	5 mM	911.0	0.126	5.50	0.987
	17.5 mM	3163.6	0.141	4.92	0.997
	20 mM	3770.4	0.212	3.27	0.954
	50 mM	9085.6	0.156	4.44	0.980
	100 mM	18482.8	0.102	6.80	0.995
NPE	0.02 mM	5.5	0.343	2.02	0.993
	0.1 mM	27.2	0.312	2.22	0.982
	0.2 mM	54.4	0.318	2.18	0.954
	1 mM	373.7	0.276	2.51	0.966
SDS	1 mM	113.0	0.16	4.33	0.997
	5 mM	631.8	0.185	3.75	0.990
	8 mM	1122.4	0.200	3.47	0.976
	20 mM	2964.0	0.170	4.08	0.945
	50 mM	6978.2	0.196	3.54	0.991
	100 mM	14620.0	0.116	5.98	0.960
Nitrate	2 mM	-	0.138	5.02	0.996
	10 mM	-	-	-	-
	100 mM	-	-	-	-
Nitrite	2 mM	-	-	-	-
	10 mM	-	-	-	-
	100 mM	-	-	-	-
Sulfate	2 mM	-	0.365	1.90	0.994
	10 mM	-	0.526	1.32	0.986
	100 mM	-	0.610	1.14	0.988
Sulfite	2 mM	-	0.136	5.10	0.953
	10 mM	-	0.140	4.95	0.918
	100 mM	-	0.139	4.99	0.940

the values predicted from the observed reduction rate constants. Once the humic acid concentration was extremely high (400 mg l⁻¹), the reduction rate would

decreased at prolonged reaction times ($t > 30$ min), which indicated that the dechlorination kinetics would deviate from the pseudo-first order kinetics. The reduction rate constants of CTC in the presence of various species of cosolutes are summarized in Table 6.2. The amphiphiles concentrations and their corresponding TOC concentrations are also listed in the table.

For dechlorination to occur, CTC was first sorbed to the Fe surface, followed by the reduction of the sorbed CTC to form dechlorination product such as methane and chlorinated byproducts (Matheson and Tratnyek, 1994). The presence of the humic acid in the dechlorination system would result in the competition between the CTC and humic acid for the adsorption sites on the metal surface. The adsorption isotherm for NOM together with the three surfactants investigated is shown in Fig. 6.3a. Basically, Fe particles were widely considered as hydrophobic particles. Nano-scale Fe particles could quickly react with water to form iron oxide. The oxidation of ZVI to iron oxide would lead iron surface to be more hydrophilic. Since the surface of the nano-scale particles were of hydrophobic and hydrophilic mixture, humic acids, which comprised both hydrophobic and hydrophilic ends, could be absorbed on the Fe surface. As shown in Fig. 6.3, the adsorption of humic acid on Pd/Fe surface tended to follow Freundlich isotherm. The sorption to Fe surfaces was believed to be non-specific surface interactions (e.g. electrostatic interaction between the amphiphiles molecule and the oxide film on Fe surface, and van der Waals force) and specific interactions (e.g. ligand exchange between carboxyl/ hydroxyl functional groups of humic acid and iron oxide surfaces) (Gu et al., 1994; Klausen et al., 2003). The accumulation of the humic acid hydrophobic and hydrophilic mixed layer on the Pd/Fe surface would form an electron transfer barrier between the Fe and the target compound. Although several researchers (Tratnyek et al., 2001; Doong and Lai, 2005) observed that specific components (e.g. quinine moieties) in the humic acid could serve as an electron mediator during the dechlorination reaction, this effect was not apparent in this study. Further analysis of the observed reduction rate constants showed that once the humic acid concentration was higher than 400 mg l^{-1} , the reduction rate constant of CTC only dropped by 70%. In groundwater, humic acid concentration (as TOC) is lower than

1 mg l⁻¹ (Tratnyek et al., 2001), while in surface water systems the humic acid concentrations usually range from 1 to 60 mg l⁻¹ in surface water systems (Alkan et al., 2007). Therefore, the influences of humic acid on the CTC dechlorination reaction were insignificant.

Fig. 6.3. Adsorption isotherm of various matrix species on the Pd/Fe surface: (a) NOM and NPE, (b) SDS and DPC.

6.3.3 Influences of anthropogenic surfactants

The observed reduction rate constants of CTC with the Pd/Fe particles in the presence of cationic surfactant DPC are shown in Fig. 6.4a. Primary study showed that DPC did not react with the Pd/Fe particles. The reduction of CTC, in the presence of DPC, still followed a pseudo-first order kinetics ($R^2 > 0.95$), as shown in Table 6.2. No deviation from this kinetic model was observed, when the DPC concentration was extremely high (100 mM). The reduction rate in 1.75 mM DPC

solution was around 25% of that in ultrapure water. With the increase of DPC concentration to 20 mM, the reactivity of the Pd/Fe particles recovered to over 60% of that in the ultrapure water. However, when the DPC concentration was further increased from 20 mM to 100 mM, the reduction rate of CTC was inhibited. The inhibition effect of DPC to the dechlorination reaction might be due to partitioning of CTC in the interior of DPC micelles. The adsorption of DPC on the Pd/Fe surface followed a linear isotherm (Fig. 6.3b). The influence of the adsorption of DPC on dechlorination reaction can be considered from following two aspects. The first one was the competition effect of DPC and CTC for the limited Fe surface adsorption sites. As shown in Table 6.2, the concentrations of DPC were usually several orders higher than that of CTC. The existence of large amount of adsorbate in the solution covering the hydrophobic adsorption site would limit CTC accessibility to the Fe surface reactive sites. The second aspect was the adsorption of DPC on the hydrophilic sites of the Fe surface, which would improve the hydrophobicity of the Fe surface. Meanwhile, for the higher DPC concentration ($\gg$ CMC), the excess amount of DPC would make CTC more readily to partition to DPC micelle, which would limit its direct contact with Fe surface. Although some researcher have proven that the surface concentration enhancement with cationic surfactant could enhance the reduction rates for chlorinated ethanes and ethenes (Alessi and Li, 2001; Li et al., 2006), this positive phenomenon was not observed for CTC in this study.

The observed reduction rate constants of CTC in the presence of NPE are shown in Fig. 6.4b. It was observed that CTC reduction kinetics would not fluctuate dramatically with the presence of the nonionic surfactant. The minor influence of NPE on the dechlorination reaction was believed to be related to the weak adsorption of NPE on the Pd/Fe particles (Fig. 6.3a). Indeed, some researchers (Porter, 1994; Paria and Khilar, 2004) argued that micelles do not adsorb on the hydrophobic surface. The adsorption of NPE on the Pd/Fe surface was negligible at NPE concentration lower than 0.2 mM. When the NPE aqueous phase concentration was increased to higher than over 5 times of CMC, the amount of NPE adsorbed on the Pd/Fe surface increased to a relatively high value. However, this adsorption

amount was still lower than those of other surfactants at the comparable aqueous phase concentrations. Therefore, the weak competition adsorption in the reduction system might be the primary reason for the weaker influence of NPE on the dechlorination reaction.

Fig. 6.4. Effect of surfactants on the reduction rate constant of CTC with the Pd/Fe particles: (a) DPC, (b) NPE, (c) SDS.

For the effect of SDS on CTC reduction with the Pd/Fe particles, it was observed that CTC reduction kinetics was more sensitive to the presence of SDS than NPE. In the SDS solution, the dechlorination rate of CTC was lower than 50% of that in the ultrapure water system, as shown in Fig. 6.4c. The adsorption of anionic SDS on the Pd/Fe particles tended to follow Langmuir isotherm (Fig. 6.3b). The dechlorination rate constant in 100 mM SDS solution was lower than the ones found at lower SDS concentrations. The drop in the reduction rate constant at extremely high SDS concentration was believed to be due to the partition of a large amount of CTC molecule in the core of SDS micelles. That the Fe surface adsorption sites were saturated by SDS molecules, which made them inaccessible to CTC, might be another possible explanation.

6.3.4 Influences of anions

(a) Nitrate and nitrite

Figure 6.5 shows the experimental results of CTC dechlorination in the presence of nitrate and nitrite. At the end of the reaction, pH value in all the solutions were over 8. According to the results observed in the preliminary experiment, the pH increases (from 7 to around 8) would not significantly inhibit the dechlorination rate. The nitrate and nitrite effects on the kinetics of CTC reduction with the Pd/Fe particles are summarized in Table 6.2. In the presence of nitrate, the CTC reduction rate decreased with the increase of the nitrate concentration. When the nitrate concentration was lower than 2 mM, CTC reduction could be completed within 30 min. However, once the nitrate concentration increased to higher than 10 mM, the reduction kinetics apparently deviated from the first-order kinetics. After 2-hour reaction, around half of CTC added remained in the 10 mM nitrate solution, while the remaining CTC amount in 100 mM nitrate solution was even higher (over 75% of initial amount). Nitrate ion was proved to be a reactive intermediate in the Fe/water system. According to the results of preliminary experiments, nitrate ion could be reduced by the Pd/Fe particles to ammonia and trace amount of nitrite. In the batch reduction systems, the metal loading in the system was only 1.2 times of the theoretical amount for CTC complete reduction. Increasing the metal loading in the system would eliminate the

inhibition effect of nitrate on the dechlorination reaction. For the sufficient Fe in the system (2.5 g l^{-1}), the fluctuation of dechlorination rate constant was around 20% for the nitrate concentration ranging from 2 mM to 100 mM. Thus, due to the continuous consumption of the Pd/Fe particles during the denitrification of nitrate ion, the insufficient amount of reductant resulted in the deviation of the CTC reduction rate from the first-order kinetics.

The presence of nitrite to the dechlorination system would lead to the almost complete deactivation of the Pd/Fe particles. During the 2-hour reaction, only lower than 20% of CTC was reduced in the nitrite solution. The higher nitrite concentrations (above 2 mM) could passivate the Fe surface and stall the dechlorination reaction.

Fig. 6.5. Experimental results of CTC reduction with Pd/Fe particles in the nitrate and nitrite solutions: (a) nitrate, (b) nitrite.

(b) Sulfate and sulfite

The effects of sulfate and sulfite on the dechlorination reaction were different from that of the nitrate and nitrite, since these two ions were supposed to be the adsorption-dominant species, which could not be reduced by Fe particles. Figure 6.6 showed the experimental results of CTC reduction with Pd/Fe particles in the presence of sulfate and sulfite. The dechlorination rate constants increased gradually with the increase of sulfate concentration, which indicated that sulfate was not a traditional believed adsorption-dominant specie. Sulfate ion promoted the corrosion of Fe particles, which led to the appearance of more reactive sites on the Fe surface. The increasing corrosion of Fe particles with the presence of sulfate ion was also reported by other researchers (Reardon, 1995; Devlin and Allin, 2005; Li and Shang, 2007). Therefore, the fresher surface condition led to the higher reactivity of the Pd/Fe particles in sulfate solution compared to the ultrapure water.

Fig. 6.6. Observed reduction rate constants of CTC with Pd/Fe particles in the sulfate and sulfite solutions.

However, sulfite showed reversed influences on the Pd/Fe system. As shown in Fig. 6.6, the introduction of sulfite would decrease the CTC dechlorination rate constants to around one half of that in the ultrapure water. For further increase of sulfite concentration to 100 mM, the dechlorination rate constant roughly remained around 50% of that in the ultrapure water. Sulfite ion was widely reported to be a Pd catalyst deactivator (Lowry and Reinhard, 2000). Despite the deactivation effect of sulfite on the Pd catalyst, the CTC dechlorination rate constants with the Pd/Fe particles were still higher than that with the nano-scale Fe particles. The residual Pd

catalyst effect in the dechlorination system indicated that sulfite ion could deactivate the external reactive sites on the Pd/Fe particles, but the internal reactive sites was still available for CTC (Schüth et al., 2000).

6.3.5 Particle ageing and regeneration

(a) Characterization of aged and regenerated nano-scale particles

Fig. 6.7 shows the SEM images and EDX spectrum of aged nano-scale Fe, Ni/Fe, and 0.2% Pd/Fe particles. For the nano-scale particles after 5-day ageing, large amount of oxygen was observed on the EDX spectrum. As indicated in the previous chapters, in the batch reduction experiments, Fe corrosion could appear in the presence of water and led to increasing pH in the aqueous phase. Amorphous $\text{Fe}(\text{OH})_2$ was the possible corrosion product, which could be transformed to magnetite or other intermediate products (e.g. green rusts) (Matheson and Tratnyek, 1994; Roh et al., 2000). SEM images of the nano-scale Fe and Ni/Fe particles (Figs. 6.6a and c) showed that the products were spheres with smooth surface. On the other hand, small amount of the aged nano-scale Pd/Fe particles revealed a green rust mineral morphology (e.g. pseudo-hexagonal form), as shown in Fig 6.7e. The most possible composition of the green rust formed over 5-day ageing could be green rust I, in the form of $[\text{Fe}_3(\text{II})\text{Fe}(\text{III})(\text{OH})_8\text{Cl}]$. The formation of green rust I was related to the CTC reduction. During CTC dechlorination, a small fraction of released chloride ion combined with the amorphous $\text{Fe}(\text{OH})_2$, forming the green rust. Green rust, as a reactive intermediate, could transform to FeOOH and Fe_3O_4 , etc. Since the transformation of green rust depended on the rate of oxidation and dehydration, different nano-scale particles showed different mineral morphologies over the aging processes.

After regeneration, although the Fe peak increased, the peak of oxygen was still very high (Figs. 6.8 b, d, and f), which indicated that the regeneration effect of sodium borohydride was limited. The mineral morphologies of the regenerated particles were similar as those of the aged particles (Fig 6.8a, c, and e). A small

fraction of Pd/Fe particles after regeneration was still in pseudo-hexagonal form, which illustrated the existence of green rust I.

Fig. 6.7. SEM images and EDX elemental mapping nano-scale particles after 5-day ageing: (a) SEM image of nano-scale Fe, (b) EDX spectrum for the Fe particles, (c) SEM images of nano-scale Ni/Fe, (d) EDX spectrum for Ni/Fe, (e) SEM image of 0.2% Pd/Fe, (f) EDX spectrum for Pd/Fe.

Fig. 6.8. SEM images and EDX spectrum for regenerated particles: (a) SEM images of nano-scale Fe; (b) EDX spectrum of nano-scale Fe; (c) SEM images of Ni/Fe; and (d) EDX spectrum of Ni/Fe; (e) SEM images of 0.2% Pd/Fe; and (f) EDX spectrum of 0.2% Pd/Fe.

Figure 6.9 shows that particle sizes of both the aged and regenerated nano-scale Pd/Fe, Ni/Fe and Fe particles were similar as those of the fresh particles (as

shown by their TEM images in Chapters 3 and 5). Meanwhile, the particle size of 5-day aged particles did not change after regeneration. It was observed that the mixed oxide particles remained spherical in shape, and the sizes of the particles were within a narrow range. The particle sizes of Ni/Fe particles were between 20 nm and 50 nm, while the particle sizes of Fe and Pd/Fe particles were between 50 nm and 100 nm. The magnetic effects between these small particles resulted in their aggregation. Although small amount of green rust I was observed in the SEM images of the aged and regenerated Pd/Fe particles, the pseudo-hexagonal form was not observed in their TEM images. The possible explanation was the instability and small amount of the green rust I formed.

The high resolution TEM (HRTEM) images of the nano-scale particles after ageing and regeneration are shown in Fig. 6.10. The Moire fringes in the images indicated the existence of the Fe crystals in the nano-scale Fe and bimetallic particles.

Fig. 6.9. TEM images of aged and regenerated nano-scale particles: (a) aged Fe, (b) regenerated Fe, (c) aged Ni/Fe, (d) regenerated Ni/Fe, (e) aged 0.2% Pd/Fe, and (f) regenerated 0.2% Pd/Fe.

Fig. 6.10. HRTEM images of aged and regenerated nano-scale particles: (a) aged Fe, (b) regenerated Fe, (c) aged Ni/Fe, (d) regenerated Ni/Fe, (e) aged 0.2% Pd/Fe, and (f) regenerated 0.2% Pd/Fe.

Fig. 6.11. XRD patterns of aged and regenerated nano-scale particles: (a) Fe, (b) Ni/Fe, and (c) 0.2% Pd/Fe.

XRD patterns of the aged and regenerated particles are shown in Fig. 6.11. The XRD patterns of the aged nano-scale Fe and nano-scale Ni/Fe and Pd/Fe

particles showed apparent peaks of oxide forms, such as Fe_3O_4 and FeOOH . In Fig. 6.11b, the peak belonged to body centered cubic (bcc) Fe was almost not observed in the XRD pattern. It indicated that the existence of Ni possibly accelerated dissolution of Fe through galvanic effect. Due to the small percentages of Pd in the Pd/Fe particles (Fig. 6.11c), peaks belonged to Pd were not noticeable on the XRD patterns. After the regeneration with sodium borohydride, the peak belonged to bcc Fe increased, while the peak belonged to fcc oxide forms decreased. The diffraction peaks belong to green rust I were not observed in the XRD pattern. It was because the green rust only existed in trace amount. The lattice parameter of the fcc Fe_3O_4 was 8.39 Å. However, regeneration with sodium borohydride could not completely eliminate the oxide forms of the particles.

(b) Reduction kinetics with the regenerated particles

The reduction rate constants of CTC with the 5-day aged particles were extremely low (figure not shown). In the presence of the aged particles, the CTC concentrations remained close to their initial values within 2 h of reaction. It was most probably due to accumulation of the oxidation film on the Fe surface, which blocked the surface reactive sites. As indicated in the previous sections, the main component of the surface oxide film was magnetite, with trace amount of green rust I as the reactive intermediate. Although magnetite could also serve as a possible electron donor in the dechlorination reaction, the reactivity of magnetite was significantly lower than that of ZVI. The half-life of CTC was in the order of hundred hours (Danielsen and Hayes, 2004). Therefore, in order to maintain the reactivity of the nano-scale particles, regeneration process should be applied to recover the reactivity of the aged particles.

The reduction results of CTC with the regenerated particles are presented in Fig. 6.12. It took around 2 h to achieve CTC complete reduction with the regenerated bimetallic particles. The reduction rate was even lower with the regenerated nano-scale Fe than those with the regenerated bimetallic particles. Around 16% CTC remained in the aqueous phase after 2 h reaction. Although the

existence of the oxide forms could inhibit the CTC reduction, the CTC reductions with the regenerated particles still followed pseudo-first order kinetics. The kinetics of CTC reduction with the regenerated particles are depicted in Table 6.3. The reactivity of the regenerated particles was around 25% of that of the fresh particles. It indicated that the sodium borohydride could partially recover the reactivity of the 5-day aged particles. Thus, regeneration of the nano-scale particles with sodium bohydride was a possible approach to recover the reactivity of the aged particles.

Fig. 6.12. Reductions of CTC with regenerated nano-scale particles as compared to those with fresh particles.

Table 6.3 Observed reduction rate constants of CTC with regenerated particles

Regenerated Particles	k_{obs} (h^{-1})	R^2	Fresh Particles	k_{obs} (h^{-1}) ^a
Fe	0.913	0.983	Fe	3.96
Ni/Fe	2.24	0.974	Ni/Fe	9.03
0.2% Pd/Fe	2.38	0.986	0.2% Pd/Fe	10.64

Note: ^a data are from Chapter 3 and 5.

6.4 Conclusions

The reduction rates of CTC increased with the decreased of pH value in the phosphate buffered system. However, the reduction rates in the buffered system

were lower than those without buffer. It indicated that phosphate would have some inhibition effect on the dechlorination reactions. Accumulation of the ferrous phosphate precipitate on the metal surface might be the possible reason.

Basically, with increasing humic acid concentration, the reduction rate of CTC with Pd/Fe particles would decrease gradually. For the extremely high humic acid concentration, CTC dechlorination would deviate from the first-order kinetics. The influences of the three types of anthropogenic surfactants followed the order: DPC (cationic) > SDS (anionic) > NPE (nonionic). The possible explanation for the minor inhibitory effects of NPE on dechlorination kinetics was related to the less adsorption of the nonionic surfactant on the particles surface. Therefore, NPE might be the most suitable surfactant for the in-situ groundwater remediation process and ex-situ soil-washing process, if the recovered water is to be treated with ZVI method. The oxyanions showed more complex influences on the dechlorination reactions than the amphiphiles. Nitrate and nitrite would inhibit the CTC dechlorination. The appearance of nitrite with relatively high concentration (>2 mM) would completely deactivate the nano-scale Pd/Fe particles. Therefore, pretreatment process should be applied to the contaminated water with significant nitrite concentration. Compared to nitrate and nitrite group, the influences of sulfate and sulfite, were weaker. Sulfite, as a catalyst toxic, would only partial deactivate the Pd reactive sites.

The particle sizes of the synthesized ZVIs did not change significantly after ageing and regeneration. Magnetite was the main component of the aged particles. SEM images showed that green rust I was a possible intermediate during the corrosion of Fe. Regeneration could partially reduce the oxide forms to their zero-valent state. After regeneration with sodium borohydride, there still existed residual amount of iron oxides. The regenerated particles could only achieve around 25% of their respective original reactivities.

CHAPTER 7.

Conclusions and Recommendations

7.1 Conclusions

In this study, nano-scale Fe particles and bimetallic particles (e.g. Ni/Fe and Pd/Fe) were synthesized with the sodium borohydride reduction method to improve the performance of conventional zero-valent Fe (ZVI) technology. Co-reduction and post-coating methods were used to prepare the Ni/Fe and Pd/Fe particles, respectively. Halogenated methanes were chosen as the target compounds to examine the reactivities of the lab-synthesized particles. The reduction kinetics, pathways and mechanisms were also proposed. The conclusions drawn from this study are listed as follows:

1. Characterization of fresh nano-scale particles and regenerated particles

Transmission electron microscope images showed that the particle sizes of the lab-synthesized particles were lower than 100 nm. The particle size of Ni/Fe particles was usually smaller than that of nano-scale Fe. Their BET surface areas were over one order higher than that of the micro-scale commercial Fe powder. The body centered cubic Fe was identified with X-ray diffraction pattern as the

dominant lattice structure in the fresh particles. After 5-day ageing, the particle sizes did not change significantly. However, the crystal structure altered to face centered cubic oxide forms. Magnetite was found to be the main corrosion component after 5-day aging. Green rust I was observed to be the possible intermediate during the corrosion of Fe. Regeneration of the aged particles with sodium borohydride could partly recover their reactivities. Thus, regeneration process could be a possible method to maintain the performance of ZVI for its long term applications.

2. Reduction kinetics and pathways of halogenated methanes

The reduction rates of halogenated methanes with the nano-scale bimetallic particles were several folds higher than those with the commercial micro-scale Fe powder. The reduction followed pseudo-first order kinetics. The reduction rate of highly halogenated methanes was higher than the less halogenated ones. Meanwhile, brominated methanes exhibited higher dehalogenation rate compared to their chlorinated counterparts. The proposed reduction pathways include both parallel and sequential pathways. Methane was identified to be the main dechlorination product. Carbon tetrachloride (CTC), carbon tetrabromide (CTB), and bromoform (BF) were mainly reduced through hydrogenolysis pathway to less halogenated products, while the predominant reduction pathway of chloroform (CF) and dibromomethane (DBM) were proposed to be reductive elimination to methane. On the other hand, the species of particles could also influence the reduction pathway of parent compounds.

3. Single-parameter linear free energy relationships and two-independent-parameter regression

Based on the linear free energy relationships (LFERs), a strong correlation existed between the observed reduction rate constants and the one-electron reduction potential (E_1). It illustrated that first electron transfer process might be the rate limiting step during reduction of the brominated methanes. The salvation of the halide ion has an important influence on the calculation of E_1 , therefore there was an offset between the brominated and chlorinated methanes in the LFERs. LFERs

analysis with E_1 , E_2 etc, should separate regressions based on the species of the halogen substitutions. For the kinetics prediction, energy of the lowest unoccupied molecular orbital (E_{LUMO}) was the more suitable descriptor, since there was only one value for each compound. Based on the statistic analysis, Pd content was identified to be another significant factor influencing the reduction kinetics.

4. Influences of solution matrix on reduction rate

Basically, reduction rate decreased with the increase of pH from 4 to 8 in the phosphate buffered solution. The reduction rate in the buffered system was lower than those in the ultra-pure water system, which indicated the inhibition effects of phosphate on the dechlorination reaction. The presence of amphiphiles (anthropogenic surfactant and natural organic matters) would inhibit the reduction of the target compounds. However, the influence of nonionic surfactant NPE on the dechlorination reaction was the weakest. Reduction of chlorinated methanes in the presence of nitrate and nitrite could be inhibited. Compared to nitrate and nitrite group, the influences of sulfate and sulfite, were weaker.

7.2 Recommendations

Both nano-scale monometallic and bimetallic ZVIs are very reactive reducing agents. The physical properties and chemical reactivity of the nano-scale particles become functions of particle size, which indicate the larger surface area, the higher reactivity of the ZVI, and the more important in future application. The medium particle size of the nano-scale particles synthesized in this study was around 50 nm. Meanwhile, the particles aggregated together to form chain structures, which will decrease the surface area of the nano-scale particles. Therefore, some particle synthesis methods used in the field of material science can be applied to reduce the particles size and eliminate the aggregation effect. In particular, template synthesis has been attracting increasing interest in recent years, since it can control the size, shape and size distribution of metallic nano-scale particles efficiently. Many organic molecules, surfactants, polymers, membrane, and dendrimers have been used as templates for preparation of nano-scale particles.

The application of template synthesis method to improve the performance of nano-scale bimetallic particles would be a challenging task.

The ability to reactivate the spent (passivated) bimetallic ZVI through cost-effective process is appealing to application of the nano-materials for environmental cleanup. Sodium borohydride is a powerful reducing agent to regenerate the oxide film-covered ZVIs. However, the optimum condition for its use in regeneration of the bimetallic particle needs future research. Apparently, the accessibility of the borohydride to the micropores of the aggregated nano-scale particles is a crucial factor. Possible improvements to the regeneration procedure used in this study may include changes in the reaction time, mixing rate, reaction temperature, pressure, etc.

The influence of solution matrix on a specific reaction is worth future study. Amphiphiles, e.g. NOM, surfactants, etc., usually appear in natural water and wastewaters. According to preliminary results of this study, the main interaction between the amphiphiles and nano-scale Fe particles was adsorption. However, the adsorption mechanism of amphiphiles and the structure of the amphiphile layer on the metal surface were still not clear. Surface specific techniques, including ellipsometry, neutron reflectivity, fluorescence spectroscopy, and atomic force microscope, can be used for in situ studies of surfactant layer property.

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Appendix A

The simulation results of CTC reduction with Ni/Fe are shown in Table A. The values of the prediction error sum of squares (PRESS) are also listed. PRESS is the squared differences between observed Y and predicted values when the observations were kept out, which is computed as

$$\text{PRESS} = \sum_i (Y_i - \hat{Y}_i)^2 \quad (\text{A.1})$$

where Y_i denotes the observed Y values, $\hat{Y}_i$ denotes the predicted values, i stands for different observations. First, the each k was set a initial value. PRESS could be calculated based on the initial k value. The procedure was repeated, until the minima PRESS was achieved.

Table A. Simulation concentration ratio of CTC reduction with Ni/Fe

$k_{\text{obs}}(\text{CT})=$	9.03	h^{-1}		$C_0=$	130 μM
$k_{11}=$	9.03	h^{-1}		PRESS(CF)=	6.456×10^{-3}
$k_{12}=$	0	h^{-1}		PRESS(DCM)=	8.620×10^{-5}
$k_{14}=$	0	h^{-1}		PRESS(CH_4)=	2.622×10^{-2}
$k_{21}=$	0.21	h^{-1}			
$k_{23}=$	0.82	h^{-1}			
t (h)	C_{CTC}/C_0	C_{CF}/C_0	C_{DCM}/C_0	C_{CH_4}/C_0	Total Mass
0	1	0	0	0	1
0.01	0.913678975	0.081715161	9.96925E-05	0.00066843	0.996162258
0.02	0.834809269	0.155615615	0.000289544	0.001941366	0.992655794
0.03	0.762747678	0.222383024	0.000560851	0.003760459	0.989452012
0.04	0.696906516	0.28264014	0.000905672	0.006072455	0.986524783
0.05	0.636748832	0.336955892	0.001316758	0.008828754	0.983850236

Appendix

0.06	0.58178402	0.385850036	0.001787495	0.011985008	0.981406558
0.07	0.531563827	0.429797396	0.002311848	0.01550075	0.979173822
0.08	0.485678693	0.469231747	0.002884311	0.019339066	0.977133817
0.0833	0.471423197	0.481781468	0.003060643	0.020521358	0.976786665
0.09	0.44375441	0.505438665	0.003492287	0.0234155	0.976100862
0.1	0.405449075	0.536993249	0.004147419	0.027808104	0.974397847
0.105	0.387554808	0.551892802	0.004484074	0.030065346	0.973997029
0.11	0.370450295	0.565954202	0.004829306	0.032380099	0.973613902
0.115	0.35410068	0.579215287	0.005182627	0.034749089	0.973247683
0.12	0.338472646	0.591712218	0.005543571	0.037169192	0.972897627
0.125	0.323534346	0.603479557	0.005911694	0.039637424	0.972563021
0.13	0.30925534	0.614550338	0.00628657	0.042150934	0.972243182
0.135	0.29560653	0.624956132	0.006667793	0.044707005	0.97193746
0.14	0.282560102	0.634727112	0.007054976	0.047303039	0.97164523
0.145	0.270089471	0.643892118	0.007447751	0.049936558	0.971365898
0.15	0.258169225	0.652478711	0.007845763	0.052605196	0.971098893
0.16	0.235883792	0.667498866	0.008660111	0.058065336	0.970108107
0.1667	0.222039292	0.676667245	0.009213219	0.061773879	0.969693635
0.17	0.215522062	0.680975494	0.00948738	0.063612104	0.96959704
0.18	0.196917976	0.692245355	0.010331919	0.069274671	0.968769922
0.19	0.179919815	0.70189003	0.011188225	0.075016132	0.968014201
0.2	0.164388952	0.710055882	0.012054493	0.080824389	0.967323715
0.21	0.150198729	0.716876582	0.012929083	0.086688439	0.966692833
0.22	0.137233421	0.722474209	0.013810501	0.092598278	0.966116409
0.23	0.125387291	0.726960246	0.014697393	0.098544813	0.965589743
0.24	0.114563732	0.730436498	0.015588525	0.104519783	0.965108539
0.25	0.104674473	0.732995929	0.01648278	0.11051569	0.964668873
0.26	0.095638865	0.734723423	0.017379143	0.116525728	0.964267159
0.27	0.08738322	0.735696484	0.018276692	0.122543725	0.963900122
0.28	0.079840211	0.735985872	0.019174595	0.128564089	0.963564768
0.29	0.072948322	0.735656186	0.020072096	0.134581757	0.963258361
0.3	0.066651349	0.734766399	0.020968511	0.140592146	0.962978405
0.3333	0.049345975	0.726848916	0.023921407	0.160391075	0.960507373
0.4	0.027023728	0.699277695	0.02961171	0.198544085	0.954457217
0.5	0.010956745	0.648234924	0.037520176	0.251569702	0.948281547
0.6	0.004442402	0.596202328	0.044793844	0.300339052	0.945777627
0.7	0.001801168	0.546461015	0.051460668	0.345039563	0.944762415

Appendix

0.8	0.000730282	0.500109949	0.05756201	0.385948557	0.944350798
0.9	0.000296092	0.457383226	0.063142085	0.423362505	0.944183908
1	0.00012005	0.418182452	0.068243911	0.45756983	0.944116243
1.1	4.86743E-05	0.382291036	0.072907862	0.488841236	0.944088808
1.2	1.97349E-05	0.349459645	0.077171269	0.517427035	0.944077685
1.3	8.00151E-06	0.319439551	0.081068432	0.543557191	0.944073175
1.4	3.24421E-06	0.291994954	0.08463077	0.567442378	0.944071346
1.5	1.31536E-06	0.266906893	0.087887034	0.589275362	0.944070605
1.6	5.33312E-07	0.243973834	0.090863515	0.609232421	0.944070304
1.7	2.16231E-07	0.223010996	0.093584249	0.627474721	0.944070182
1.8	8.76705E-08	0.203849246	0.09607121	0.644149589	0.944070133
1.9	3.55459E-08	0.186333892	0.098344484	0.659391701	0.944070113
2	1.44121E-08	0.170323496	0.10042243	0.673324163	0.944070105
2.1	5.84336E-09	0.155688758	0.102321833	0.686059504	0.944070101
2.2	2.36918E-09	0.142311481	0.104058033	0.697700583	0.9440701
2.3	9.60584E-10	0.130083622	0.105645053	0.708341423	0.944070099
2.4	3.89468E-10	0.118906419	0.107095712	0.718067968	0.944070099
2.5	1.57909E-10	0.108689597	0.108421725	0.726958777	0.944070099
2.6	6.40242E-11	0.099350637	0.109633803	0.73508566	0.944070099
2.7	2.59586E-11	0.090814111	0.110741735	0.742514254	0.944070099
2.8	1.05249E-11	0.08301107	0.11175447	0.749304559	0.944070099
2.9	4.2673E-12	0.075878492	0.112680187	0.75551142	0.944070099
3	1.73017E-12	0.069358768	0.113526364	0.761184967	0.944070099